PCT/EP2004/006442

EP04/6442

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Signed Stephen Hurdle

Dated 14 April 2004

PCT/EP2004/006442

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THE PATENT OFFICE
16 JUN 2003
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Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

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1. Your reference — 16 JUN 2003 — PI-70282P1

17JUN03 E815441-1 D02093
P01/7700 0.00-0313937.5

2. Patent application number *(The Patent Office will fill in this part)* 0313937.5

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

SYNGENTA PARTICIPATIONS AG
Intellectual Property Department
Schwarzwaldallee 215
4058 Basel, SWITZERLAND

Patents ADP number *(if you know it)*

If the applicant is a corporate body, give the country/state of its incorporation — 8029555001

4. Title of the invention — Avermectin B1 monosaccharide derivatives having an aminosulfonyloxy substituent in the 4'-position

5. Name of your agent *(if you have one)* — Michael James RICKS

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Syngenta Limited
Intellectual Property Department
Jealott's Hill Research Centre
PO Box 3538, BRACKNELL
Berkshire, RG42 6YA, UNITED KINGDOM

Patents ADP number *(if you know it)* — 01282433003 — 8029563001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

Yes

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	
Description	45
Claim(s)	4
Abstract	1
Drawing(s)	

10. If you are also filing any of the following, state how many against each item.

Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature SYNGENTA PARTICIPATIONS AG Joanna Chandler Date 16/6/03

Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

Joanna Carmen CHANDLER 01344 414079

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Notes

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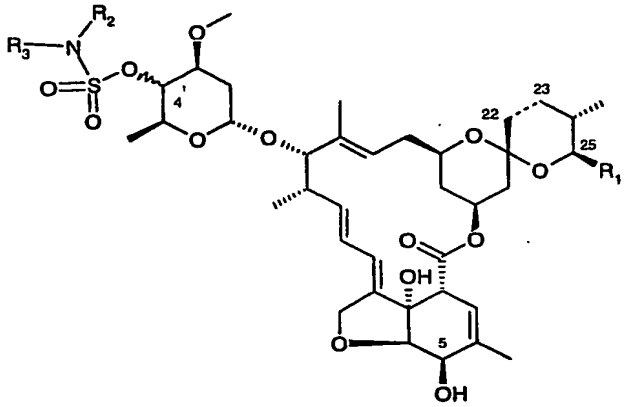
Avermectin B1 monosaccharide derivatives having an aminosulfonyloxy substituent in the 4'-position

The invention relates to (1) a compound of formula



(I)

wherein the bond between carbon atoms 22 and 23 may be a single or a double bond;

R_1 is C_1-C_{12}alkyl, C_3-C_8cycloalkyl; or C_2-C_{12}alkenyl;

R_2 and R_3 are independently of each other hydrogen, C_1-C_{12}alkyl, C_3-C_{12}cycloalkyl, C_2-C_{12}alkenyl, C_2-C_{12}alkynyl, aryl or heteroaryl; wherein the C_1-C_{12}alkyl, C_3-C_{12}cycloalkyl, C_2-C_{12}alkenyl, C_2-C_{12}alkynyl, aryl and heteroaryl radicals may be unsubstituted or mono- to penta-substituted; -C(=O)R_4 or SO_2R_4; or

R_2 and R_3 together are a three- to seven-membered alkylene bridge or a four- to seven-membered alkenylene bridge wherein one or two CH_2 groups in the alkylene or alkenylene may have been replaced by O, S or NR_5; or are a group $=N^+=N^-$,

and wherein the substituents of the alkyl, alkenyl, alkynyl, alkylene, alkenylene, cycloalkyl, aryl and heteroaryl radicals defined under R_2 and R_3 are selected from the group consisting of OH, =O, SH, =S, -NH_2, CN, NO_2, halogen, C_1-C_{12}alkyl, halo-C_1-C_2alkyl, C_1-C_{12}alkenyl, C_2-C_6alkynyl; C_3-C_8cycloalkyl which is unsubstituted or substituted by from one to three methyl groups; norbornenyl; C_3-C_8cycloalkenyl that is unsubstituted or substituted by from one to three methyl groups; C_3-C_8halocycloalkyl, C_1-C_{12}alkoxy, C_1-C_6-alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_{12}alkenyloxy, C_2-C_{12}alkenyloxy-C_1-C_6alkoxy, C_3-C_8cycloalkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_3-C_8cycloalkylthio, C_1-C_{12}haloalkylthio, C_1-C_{12}alkylsulfinyl, C_3-C_8cycloalkyl-sulfinyl, C_1-C_{12}haloalkylsulfinyl, C_3-C_8halocycloalkylsulfinyl, C_1-C_{12}alkylsulfonyl, C_3-C_8cyclo-

alkylsulfonyl, C_1-C_{12}haloalkylsulfonyl, C_3-C_8halocycloalkylsulfonyl, C_2-C_8alkenyl, C_2-C_8alkynyl, -NH(C_1-C_6alkyl), -N(C_1-C_6alkyl)$_2$, -C(=O)R_6, -NHC(=O)R_7, -P(=O)(OC_1-C_6alkyl)$_2$, aryl, heterocyclyl, aryloxy and heterocyclyloxy; wherein the aryl, heterocyclyl, aryloxy and heterocyclyloxy radicals are unsubstituted or, depending upon the possibilities of substitution at the ring, mono- to penta-substituted by substituents selected from the group consisting of OH, halogen, CN, NO_2, C_1-C_{12}alkyl, C_3-C_8cycloalkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_{12}alkylsulfinyl, C_1-C_{12}alkylsulfonyl, C_1-C_6alkoxy-C_1-C_6alkyl, dimethylamino-C_1-C_6alkoxy, C_2-C_8alkenyl, C_2-C_8alkynyl, phenoxy, phenyl-C_1-C_6alkyl; phenoxy that is unsubstituted or substituted by from one to three substituents selected independently of one another from halogen, methoxy, trifluoromethyl and trifluoromethoxy; phenyl-C_1-C_6alkoxy that is unsubstituted or substituted in the aromatic ring by from one to three substituents selected independently of one another from halogen, methoxy, trifluoromethyl and trifluoromethoxy; phenyl-C_2-C_6alkenyl, phenyl-C_2-C_6alkynyl, methylenedioxy, -C(=O)R_6, -O-C(=O)R_7, -NH-C(=O)R_7, -NH_2, -NH(C_1-C_{12}alkyl), -N(C_1-C_{12}alkyl)$_2$, C_1-C_6alkylthio, C_1-C_6alkylsulfinyl, C_3-C_8cycloalkylsulfinyl, C_1-C_6haloalkylsulfinyl, C_3-C_8halocycloalkylsulfinyl, C_1-C_6alkylsulfonyl, C_3-C_8cycloalkylsulfonyl, C_1-C_6haloalkylsulfonyl and C_3-C_8halocycloalkylsulfonyl;

R_4 is H, C_1-C_8alkyl, C_1-C_8alkyl that is mono- to hepta-substituted by halogen, nitro, C_1-C_8alkoxy, aryloxy, OH, SH, -NH_2, -NH(C_1-C_{12}alkyl) or -N(C_1-C_{12}alkyl)$_2$; C_1-C_8alkoxy, halo-C_1-C_8alkoxy, C_3-C_8cycloalkyl, C_3-C_8cycloalkoxy, C_2-C_8alkenyl, halo-C_2-C_8alkenyl, C_2-C_8alkenyloxy, halo-C_2-C_8alkenyloxy, C_2-C_8alkynyl, C_2-C_8alkynyloxy, -NH_2, -NH(C_1-C_{12}alkyl), -N(C_1-C_{12}alkyl)$_2$, aryl, aryloxy, benzyl, benzyloxy, heterocyclyl, heterocyclyloxy, heterocyclylmethyl, heterocyclylmethoxy, -NH-aryl, -NH-heterocyclyl, -N(C_1-C_6alkyl)-aryl or -N(C_1-C_6alkyl)-heterocyclyl; wherein the radicals aryl, aryloxy, benzyl, benzyloxy, heterocyclyl, heterocyclyloxy, heterocyclylmethyl, heterocyclylmethoxy, -NH-aryl, -NH-heterocyclyl, -N(C_1-C_6alkyl)-aryl and -N(C_1-C_6alkyl)-heterocyclyl are unsubstituted or, depending upon the possibilities of substitution at the ring, are in the ring substituted by from one to three substituents selected independently of one another from halogen, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_{12}alkylsulfinyl, C_1-C_{12}alkylsulfonyl, C_2-C_8alkenyloxy, C_2-C_8alkynyloxy, nitro, -N_3, and cyano;

R_5 is C_1-C_8alkyl, C_3-C_8cycloalkyl, C_2-C_8alkenyl, C_2-C_8alkynyl, benzyl, -C(=O)-R_8 or -C(=S)-R_8;

R_6 is H, OH, SH, C_1-C_8alkyl, C_1-C_8alkyl which is mono- to hepta-substituted by halogen, nitro, C_1-C_8alkoxy, aryloxy, OH, SH, $-NH_2$, $-NH(C_1$-C_{12}alkyl) or $-N(C_1$-C_{12}alkyl)$_2$; C_1-C_8alkoxy, halo-C_1-C_8alkoxy, C_3-C_8cycloalkyl, C_3-C_8cycloalkoxy, C_2-C_8alkenyl, C_2-C_8alkenyloxy, C_2-C_8alkynyl, C_2-C_8alkynyloxy, $-NH_2$, $-NH(C_1$-C_{12}alkyl), $-N(C_1$-C_{12}alkyl)$_2$, aryl, aryloxy, benzyl, benzyloxy, heterocyclyl, heterocyclyloxy, heterocyclylmethyl or heterocyclylmethoxy; wherein the radicals aryl, aryloxy, benzyl, benzyloxy, heterocyclyl, heterocyclyloxy, heterocyclylmethyl and heterocyclylmethoxy are unsubstituted or, depending upon the possibilities of substitution at the ring, are substituted by from one to three substituents selected independently of one another from halogen, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_{12}alkylsulfinyl, C_1-C_{12}alkylsulfonyl, C_2-C_8alkenyloxy, C_2-C_8alkynyloxy, nitro, $-N_3$, and cyano;

R_7 is H, C_1-C_{12}alkyl, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_{12}haloalkyl, C_2-C_8alkenyl, C_2-C_8alkynyl, aryl, heterocyclyl, benzyl, $-NH_2$, $-NH(C_1$-C_{12}alkyl), $-N(C_1$-C_{12}alkyl)$_2$, -NH-phenyl or $-N(C_1$-C_{12}alkyl)-phenyl; and

R_8 is H, OH, SH, $-NH_2$, $-NH(C_1$-C_{12}alkyl), $-N(C_1$-C_{12}alkyl)$_2$, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_{12}alkylthio, C_1-C_{12}alkylsulfinyl, C_1-C_{12}alkylsulfonyl, C_2-C_8alkenyloxy, C_2-C_8alkynyloxy; phenyl, phenoxy, benzyloxy, -NH-phenyl, $-N(C_1$-C_6alkyl)-phenyl, -NH-C_1-C_6alkyl-C(=O)-R_9, $-N(C_1$-C_6alkyl)-C_1-C_6alkyl-C(=O)-R_9; or phenyl, phenoxy, benzyloxy, -NH-phenyl or $-N(C_1$-C_6alkyl)—phenyl each of which is substituted in the aromatic ring by from one to three substituents selected independently of one another from halogen, C_1-C_6alkoxy, C_1-C_6haloalkyl and C_1-C_6haloalkoxy;

R_9 is H, OH, C_1-C_{12}alkyl, C_1-C_{12}alkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy, C_2-C_8alkenyloxy, phenyl, phenoxy, benzyloxy, $-NH_2$, $-NH(C_1$-C_{12}alkyl), $-N(C_1$-C_{12}alkyl)$_2$, -NH-phenyl or $-N(C_1$-C_{12}alkyl)-phenyl;

and, where applicable, to E/Z isomers, mixtures of E/Z isomers, diastereomers and/or tautomers, in each case in free form or in salt form;

to a process for the preparation of and to the use of those compounds and their isomers and tautomers; to starting materials for the preparation of the compounds of formula (I); to pesticidal compositions in which the active ingredient has been selected from the compounds of formula (I) and their tautomers; and to a method of controlling pests using those compositions.

Hereinbefore and hereinafter, the bond marked by the symbol ~~ in formulae (I), (II) and (IV) indicates that the 4'-*(S)*- as well as the 4'-*(R)*-isomer is meant.

Certain macrolide compounds are proposed for pest control in the literature. The biological properties of those known compounds are not entirely satisfactory, however, for which reason there is a need to provide further compounds having pesticidal properties, especially for the control of insects and members of the order Acarina. That problem is solved according to the invention by the provision of the present compounds of formula (I).

The compounds claimed according to the invention are derivatives of avermectin. Avermectins are known to the person skilled in the art. They are a group of structurally closely related pesticidally active compounds which are obtained by fermentation of a strain of the microorganism *Streptomyces avermitilis*. Derivatives of avermectins can be obtained *via* conventional chemical syntheses.

The Avermectins which can be obtained from Streptomyces avermitilis are referred to as A1a, A1b, A2a, A2b, B1a, B1b, B2a and B2b. The compounds referred to as "A" and "B" have a methoxy radical and an OH group, respectively, in the 5-position. The "a" series and the "b" series are compounds in which the substituent R_1 (in position 25) is a sec-butyl radical and an isopropyl radical, respectively. The number 1 in the name of the compounds means that carbon atoms 22 and 23 are linked by double bonds; the number 2 means that they are linked by a single bond and that the C atom 23 carries an OH group. The above nomenclature is adhered to in the description of the present invention to denote the specific structure type in the not naturally occurring Avermectin derivatives according to the invention which corresponds to the naturally occurring Avermectin. What is claimed according to the invention are the monosaccharide derivatives of compounds of the B1 series, in particular mixtures of the monosaccharide derivatives of Avermectin B1, especially B1a and B1b, along with derivatives having a single bond between carbon atoms 22 and 23, and derivatives having other substituents in the 25-position.

Some of the compounds of formula (I) may be in the form of tautomers. Accordingly, any reference to the compounds of formula (I) hereinbefore and hereinafter is to be understood, where applicable, as including also corresponding tautomers, even if the latter are not specifically mentioned in every case.

The compounds of formula (I) and, where applicable, their tautomers can form salts, for example acid addition salts. These acid addition salts are formed, for example, with strong inorganic acids, such as mineral acids, for example sulfuric acid, a phosphoric acid or

a hydrohalic acid, with strong organic carboxylic acids, such as unsubstituted or substituted, for example halo-substituted, C_1-C_4alkanecarboxylic acids, for example acetic acid, unsaturated or saturated dicarboxylic acids, for example oxalic acid, malonic acid, maleic acid, fumaric acid or phthalic acid, hydroxycarboxylic acids, for example ascorbic acid, lactic acid, malic acid, tartaric acid or citric acid, or benzoic acid, or with organic sulfonic acids, such as unsubstituted or substituted, for example halo-substituted, C_1-C_4alkane- or aryl-sulfonic acids, for example methane- or p-toluene-sulfonic acid. Compounds of formula (I) that have at least one acidic group can furthermore form salts with bases. Suitable salts with bases are, for example, metal salts, such as alkali metal salts or alkaline earth metal salts, for example sodium, potassium or magnesium salts, or salts with ammonia or with an organic amine, such as morpholine, piperidine, pyrrolidine, a mono-, di- or tri-lower alkylamine, for example ethylamine, diethylamine, triethylamine or dimethylpropylamine, or a mono-, di- or trihydroxy-lower alkylamine, for example mono-, di- or tri-ethanolamine. Corresponding internal salts may also be formed where appropriate. The free form is preferred. Among the salts of the compounds of formula (I), the agrochemically advantageous salts are preferred. Hereinbefore and hereinafter, any reference to the free compounds of formula (I) or their salts is to be understood as including, where appropriate, also the corresponding salts or the free compounds of formula (I), respectively. The same applies to tautomers of compounds of formula (I) and salts thereof.

Unless defined otherwise, the general terms used hereinbefore and hereinafter have the meanings given below.

Unless defined otherwise, carbon-containing groups and compounds each contain from 1 up to and including 6, preferably from 1 up to and including 4, especially 1 or 2, carbon atoms.

Halogen - as a group *per se* and as a structural element of other groups and compounds, such as haloalkyl, haloalkoxy and haloalkylthio - is fluorine, chlorine, bromine or iodine, especially fluorine, chlorine or bromine, more especially fluorine or chlorine.

Alkyl - as a group *per se* and as a structural element of other groups and compounds, such as haloalkyl, alkoxy and alkylthio - is, in each case giving consideration to the number of carbon atoms contained in the group or compound in question, either straight-chained, i.e. methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl or octyl, or branched, e.g. isopropyl, isobutyl, sec-butyl, tert-butyl, isopentyl, neopentyl or isohexyl.

Cycloalkyl - as a group *per se* and as a structural element of other groups and compounds, such as halocycloalkyl, cycloalkoxy and cycloalkylthio - is, in each case giving due consideration to the number of carbon atoms contained in the group or compound in question, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl or cyclooctyl.

Alkenyl - as a group *per se* and as a structural element of other groups and compounds - is, giving due consideration to the number of carbon atoms and conjugated or isolated double bonds contained in the group in question, either straight-chained, e.g. vinyl, allyl, 2-butenyl, 3-pentenyl, 1-hexenyl, 1-heptenyl, 1,3-hexadienyl or 1,3-octadienyl, or branched, e.g. isopropenyl, isobutenyl, isoprenyl, tert-pentenyl, isohexenyl, isoheptenyl or isooctenyl. Alkenyl groups having from 3 to 12, especially from 3 to 6, more especially 3 or 4, carbon atoms are preferred.

Alkynyl - as a group *per se* and as a structural element of other groups and compounds - is, in each case giving due consideration to the number of carbon atoms and conjugated or isolated double bonds contained in the group or compound in question, either straight-chained, e.g. ethynyl, propargyl, 2-butynyl, 3-pentynyl, 1-hexynyl, 1-heptynyl, 3-hexen-1-ynyl or 1,5-heptadien-3-ynyl, or branched, e.g. 3-methylbut-1-ynyl, 4-ethylpent-1-ynyl, 4-methylhex-2-ynyl or 2-methylhept-3-ynyl. Alkynyl groups having from 3 to 12, especially from 3 to 6, more especially 3 or 4, carbon atoms are preferred.

Alkylene and alkenylene are straight-chained or branched bridge members, especially $-CH_2-CH_2-CH_2-$, $-CH_2-CH_2-CH_2-CH_2-$, $-CH_2-CH_2-CH_2-CH_2-CH_2-$, $-CH_2(CH_3)CH_2-CH_2-$, $-CH_2C(CH_3)_2-CH_2-$, $-CH_2-CH=CH-CH_2-$ or $-CH_2-CH=CH-CH_2-CH_2-$.

Halo-substituted carbon-containing groups and compounds, such as alkyl, alkenyl, alkynyl, cycloalkyl, alkoxy or alkylthio substituted by halogen, may be partially halogenated or perhalogenated, it being possible in the case of polyhalogenation for the halogen substituents to be the same or different. Examples of haloalkyl - as a group *per se* and as a structural element of other groups and compounds, such as haloalkoxy and haloalkylthio - are methyl substituted from one to three times by fluorine, chlorine and/or bromine, such as CHF_2 or CF_3; ethyl substituted from one to five times by fluorine, chlorine and/or bromine, such as CH_2CF_3, CF_2CF_3, CF_2CCl_3, CF_2CHCl_2, CF_2CHF_2, CF_2CFCl_2, CF_2CHBr_2, CF_2CHClF, CF_2CHBrF or CClFCHClF; propyl or isopropyl substituted from one to seven times by fluorine, chlorine and/or bromine, such as $CH_2CHBrCH_2Br$, CF_2CHFCF_3, $CH_2CF_2CF_3$, $CH(CF_3)_2$ or $CF(CF_3)_2$, butyl or an isomer thereof substituted from one to nine times by fluorine, chorine and/or bromine, such as $CF(CF_3)CHFCF_3$ or $CH_2(CF_2)_2CF_3$; pentyl or an

isomer thereof substituted from one to eleven times by fluorine, chlorine and/or bromine, such as $CF(CF_3)(CHF)_2CF_3$ or $CH_2(CF_2)_3CF_3$; and hexyl or an isomer thereof substituted from one to thirteen times by fluorine, chlorine and/or bromine, such as $(CH_2)_4CHBrCH_2Br$, $CF_2(CHF)_4CF_3$, $CH_2(CF_2)_4CF_3$ or $C(CF_3)_2(CHF)_2CF_3$.

Aryl is especially phenyl, naphthyl, anthracenyl or perylenyl, preferably phenyl.

Heterocyclyl is understood as being a three- to seven-membered monocyclic ring, which may be saturated or unsaturated, and that contains from one to three hetero atoms selected from the group consisting of N, O and S, especially N and S; or a bicyclic ring-system having from 8 to 14 ring atoms, which may be saturated or unsaturated, and that may contain either in only one ring or in both rings independently of one another, one or two hetero atoms selected from N, O and S.

Heterocyclyl is especially pyridyl, pyrimidyl, s-triazinyl, 1,2,4-triazinyl, thienyl, furyl, tetrahydrofuranyl, pyranyl, tetrahydropyranyl, pyrrolyl, pyrazolyl, imidazolyl, thiazolyl, triazolyl, tetrazolyl, oxazolyl, thiadiazolyl, oxadiazolyl, benzothienyl, quinolinyl, quinoxalinyl, benzofuranyl, benzimidazolyl, benzopyrrolyl, benzothiazolyl, indolyl, coumarinyl or indazolyl, which are preferably bonded *via* a carbon atom; preference is given to thienyl, thiazolyl, benzofuranyl, benzothiazolyl, furyl, tetrahydropyranyl and indolyl; especially pyridyl or thiazolyl.

Within the scope of the present invention, preference is given to

(2) compounds according to group (1) of formula (I) wherein R_2 is H, C_1-C_8alkyl, C_1-C_8-alkyl mono- to penta-substituted by halogen, OH, C_1-C_4alkoxy or CN; C_3-C_{12}alkenyl, C_3-C_{12}alkynyl or $C(=O)R_4$;

(3) compounds according to anyone of groups (1) or (2) of formula (I) wherein R_2 is C_1-C_4alkyl, especially methyl;

(4) compounds according to group (2) of formula (I) wherein R_2 is ethyl;

(5) compounds according to group (2) of formula (I) wherein R_2 is n-propyl;

(6) compounds according to anyone of groups (1) to (5) of formula (I) wherein R_3 is H, C_1-C_8alkyl, C_1-C_8alkyl substituted by halogen, OH or CN; C_3-C_{12}alkenyl or C_3-C_{12}alkynyl;

(7) compounds according to anyone of groups (1) to (5) of formula (I) wherein R_3 is H;

(8) compounds according to anyone of groups (1) to (5) of formula (I) wherein R_3 is methyl;

(9) compounds according to anyone of groups (1) to (5) of formula (I) wherein R_3 is ethyl;

(10) compounds according to anyone of groups (1) to (5) of formula (I) wherein R_3 is n-propyl;

(11) compounds according to anyone of groups (1) to (5) of formula (I) wherein R_3 is isopropyl;

(12) compounds according to anyone of groups (2) and (6) to (11) of formula (I) wherein R_2 is $-C(=O)R_4$ and R_4 is H, C_1-C_4alkyl, C_1-C_4alkoxy, halo-C_1-C_4alkyl, halo-C_1-C_4alkoxy, C_3-C_8cycloalkoxy, C_2-C_8alkenyloxy, C_2-C_8alkynyloxy, $-NH_2$, $-NH(C_1$-C_{12}alkyl), $-N(C_1$-C_{12}alkyl)$_2$, aryl, aryloxy, benzyl or benzyloxy; wherein the radicals aryl, aryloxy, benzyl and benzyloxy are unsubstituted or substituted by from one to three substituents selected independently of one another from halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, C_1-C_{12}haloalkylthio, nitro and cyano;

(13) compounds according to group (1) of formula (I) wherein R_2 and R_3 together are $-CH_2-CH_2-CH_2-$ or $-CH_2-CH_2-CH_2-CH_2-$;

(14) compounds according to group (1) of formula (I) wherein R_2 and R_3 together are $-CH_2-CH_2-O-CH_2-CH_2-$ or $-CH_2-CH_2-N(CH_3)-CH_2-CH_2-$;

(15) compounds according to anyone of groups (1) and (6) to (11) of formula (I) wherein R_2 is substituted C_1-C_4alkyl, especially $-CH_2-$, and the substituents are selected from the group consisting of OH, CN, halogen, C_3-C_8cycloalkyl; C_3-C_8cycloalkenyl that is unsubstituted or substituted by from one to three methyl groups; C_1-C_{12}alkoxy, C_2-C_8alkynyl, $-C(=O)R_6$, $-NHC(=O)R_7$, $-P(=O)(OC_1$-C_6alkyl)$_2$; and phenyl, naphthyl, anthracenyl, phenanthrenyl, fluorenyl, perylenyl and heterocyclyl which are unsubstituted or, depending upon the possibilities of substitution at the ring, mono- to penta-substituted;

especially wherein the substituents of R_2 are selected from the group consisting of halogen, CN, C_3-C_8cycloalkyl, C_2-C_8alkynyl, $-C(=O)R_6$, $-NHC(=O)R_7$, $-P(=O)(OC_1$-C_6alkyl)$_2$; and phenyl, naphthyl, anthracenyl, pyridyl, thiazolyl, imidazolyl, furyl, quinolinyl and pyrazolyl which are unsubstituted or, depending upon the possibilities of substitution at the ring, mono- to tri-substituted;

(16) compounds according to anyone of groups (1) to (5) of formula (I) wherein R_2 is benzyl that unsubstituted or carries on the aromatic moiety from one to three substituents that are selected from the group consisting of halogen, CN, NO_2, C_1-C_{12}alkyl, C_3-C_8cyclo-

alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_{12}alkylsulfinyl, C_1-C_{12}alkylsulfonyl, C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_8alkenyl, C_2-C_8alkynyl, phenoxy, phenyl-C_1-C_6alkyl; methylenedioxy, -C(=O)R_6, -O-C(=O)R_7, -NH-C(=O)R_7, -NH_2, -NH(C_1-C_{12}alkyl), -N(C_1-C_{12}alkyl)$_2$, C_1-C_6alkylthio, C_1-C_6alkylsulfinyl, C_3-C_8cycloalkylsulfinyl, C_1-C_6haloalkylsulfinyl, C_3-C_8halocycloalkylsulfinyl, C_1-C_6alkylsulfonyl, C_3-C_8cycloalkylsulfonyl, C_1-C_6haloalkylsulfonyl and C_3-C_8halocycloalkylsulfonyl;

R_6 is H, OH, SH, C_1-C_8alkyl, C_1-C_8alkyl which is mono- to hepta-substituted by halogen, nitro, C_1-C_8alkoxy, aryloxy, OH, SH, -NH_2, -NH(C_1-C_{12}alkyl) or -N(C_1-C_{12}alkyl)$_2$; C_1-C_8alkoxy, halo-C_1-C_8alkoxy, C_3-C_8cycloalkyl, C_3-C_8cycloalkoxy, -NH_2, -NH(C_1-C_{12}alkyl), -N(C_1-C_{12}alkyl)$_2$, aryl, aryloxy, benzyl, benzyloxy, heterocyclyl, heterocyclyloxy, heterocyclylmethyl or heterocyclylmethoxy;

R_7 is H, C_1-C_{12}alkyl, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_{12}haloalkyl, aryl, heterocyclyl, benzyl, -NH_2, -NH(C_1-C_{12}alkyl), -N(C_1-C_{12}alkyl)$_2$, -NH-phenyl or -N(C_1-C_{12}alkyl)-phenyl;

(17) compounds according to anyone of groups (1) and (6) to (11) of formula (I) wherein R_2 is C_1-C_4alkyl-C(=O)R_6, especially -CH_2-C(=O)R_6; and

R_6 is H, OH, -NH_2, -NH(C_1-C_2alkyl), -N(C_1-C_2alkyl)$_2$, C_1-C_4alkyl, C_1-C_{12}alkoxy, C_2-C_4alkenyloxy, phenyl, phenoxy, benzyloxy, -NH-phenyl, -NH-C_1-C_2alkyl-C(=O)-O-C_1-C_2-alkyl-phenyl, -P(=O)(OC_1-C_6alkyl)$_2$; or phenyl, phenoxy, benzyloxy or NH-phenyl substituted by chlorine, fluorine, methoxy, trifluoromethyl or trifluoromethoxy;

more especially wherein R_6 is C_1-C_{12}alkoxy;

(18) compounds according to anyone of groups (1) to (18) of formula (I) that have the R configuration at the 4'-position;

(19) compounds according to anyone of groups (1) to (18) of formula (I) that have the S configuration at the 4'-position;

(20) compounds according to anyone of groups (1) to (18) of formula (I) wherein R_1 is isopropyl or sec-butyl, preferably wherein a mixture of the isopropyl and the sec-butyl derivative is present;

(21) compounds according to anyone of groups (1) to (20) of formula (I) wherein R_1 is cyclohexyl;

(22) compounds according to anyone of groups (1) to (20) of formula (I) wherein R_1 is 1-methyl-butyl;

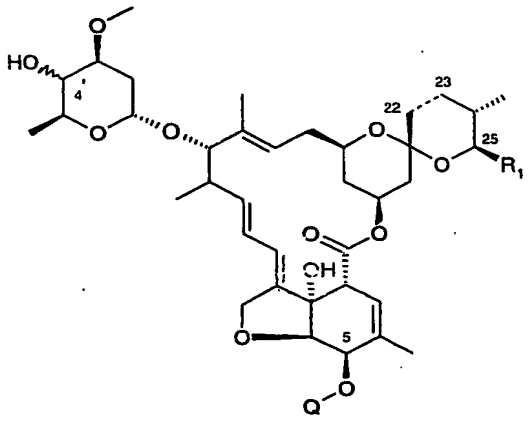
(23) compounds according to anyone of groups (1) to (22) of formula (I) wherein the bond between carbon atoms 22 and 23 is a single bond;

(24) compounds according to anyone of groups (1) to (22) of formula (I) wherein the bond between carbon atoms 22 and 23 is a double bond.

Special preference is given within the scope of the invention to compounds A.1 to A.29 and to the compounds of formula (I) listed in the Tables 1 to 36 and, where applicable, their E/Z isomers and mixtures of E/Z isomers.

The invention further relates to a process for the preparation of the compounds of formula (I) as defined above under (1) and, where applicable, tautomers thereof, which comprises

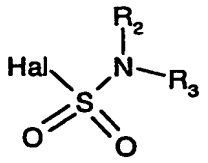
(A) reacting a compound of formula



(II),

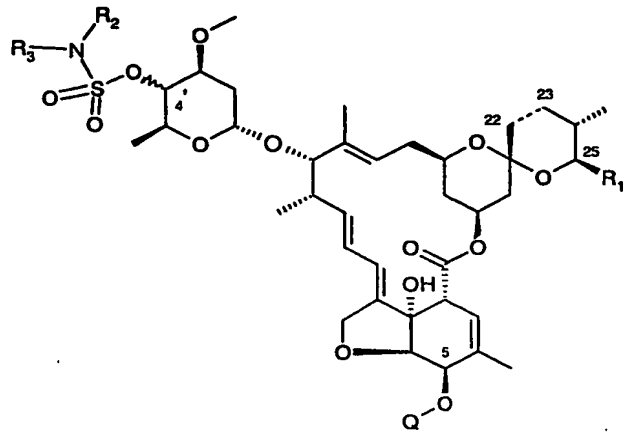
wherein the bond marked by ~~ indicates the S- as well as the R-isomer at the 4'-position; wherein R_1 is as defined above under (1) for formula (I), the bond between the carbon atoms 22 and 23 may be a single or a double bond;

and Q is a protecting group, and which is known or can be prepared by methods known *per se*, with a compound of formula



(III)

wherein R_2 and R_3 are as defined above for formula (I) and Hal is a halogen atom, preferably chlorine, bromine or iodine, and which is known or can be prepared by methods known *per se*, to form a compound of formula



(IV),

wherein the bond between the carbon atoms 22 and 23 may be a single or a double bond; Q, R_1, R_2 and R_3 are as defined for formula (II); and

(B) removing the protecting group Q of the compound of formula (IV) so obtained; or

(C) reacting a compound of formula (I) wherein R_1 and R_3 are as defined for formula (I) and R_2 is H, with a compound of the formula Hal-R_2 wherein R_2 is as defined for formula (I) and Hal is halogen, especially chlorine, bromine or iodine; or

(D) reacting a compound of formula (IV) wherein Q, R_1 and R_3 are as defined for formula (IV) and R_2 is H, with a compound of the formula Hal-R_2 wherein R_2 is as defined for formula (I) and Hal is halogen, especially chlorine, bromine or iodine; and removing the protecting group Q from the compound of formula (IV) so obtained analogously to process step (B); or

(E) for the preparation of a compound of formula (I) wherein R_1 is as defined for formula (I) and R_2 and R_3 are identical and, with the exception of hydrogen, are as defined for formula (I), reacting a compound of formula (I) wherein R_1 is as defined for formula (I) and R_2 and R_3 are H, with two moles of a compound of the formula Hal-R_2 wherein R_2 is as defined for formula (I) and Hal is halogen, especially chlorine, bromine or iodine; or reacting a compound of formula (IV) wherein R_1 is as defined for formula (IV) and R_2 and R_3 are H, with two moles of a compound of the formula Hal-R_2 wherein R_2 is as defined for formula (I) and Hal is halogen, especially bromine or iodine; and then removing the protecting group Q analogously to process step (B); or

(F) for the preparation of a compound of formula (I) wherein R_1 is as defined for formula (I) and R_2 and R_3 together are a three- to seven-membered alkylene bridge or a four- to seven-membered alkenylene bridge wherein one CH_2 group in the alkylene or

alkenylene may have been replaced by O, S or NR_5, reacting a compound of formula (I) wherein R_1 is as defined for formula (I) and R_2 and R_3 are H, with one mole of a compound of the formula Hal-A-Hal wherein the bridge member A has the above-mentioned definition of R_2 and R_3 together and Hal is halogen, especially chlorine, bromine or iodine; or, analogously to process step (E), reacting a compound of formula (IV) wherein R_1 and Q are as defined for formula (IV) and R_2 and R_3 are H, with one mole of a compound of the formula Hal-A-Hal as defined above, and then removing the protecting group Q analogously to process step (B); or

(G) for the preparation of a compound of formula (I) wherein R_2 is $-C(O)R_4$ and R_1, R_3 and R_4 are as defined for formula (I), either reacting a compound of formula (I) wherein R_1 and R_3 are as defined for formula (I) and R_2 is H, with a compound of the formula Hal-$C(O)R_4$ wherein R_4 is as defined above for formula (I) and Hal is halogen; or reacting a compound of formula (IV) wherein R_1, R_3, R_4 and Q are as defined for formula (I) and R_2 is H, with a compound of the formula Hal-$C(O)R_4$ wherein R_4 is as defined above for formula (I) and Hal is halogen; and then removing the protecting group Q.

The remarks made above regarding tautomers of compounds of formula (I) apply analogously to the starting materials mentioned hereinbefore and hereinafter with regard to their tautomers.

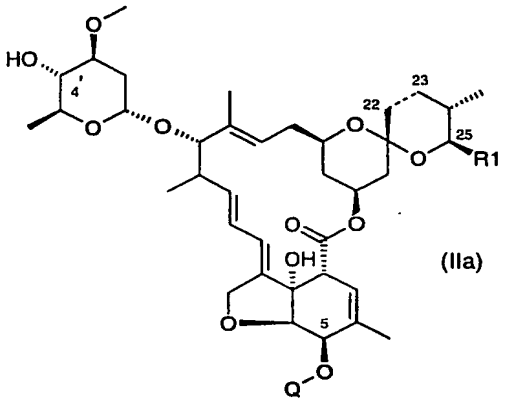
The reactions described hereinbefore and hereinafter are carried out in a manner known *per se*, for example in the absence or, customarily, in the presence of a suitable solvent or diluent or of a mixture thereof, the reactions being carried out, as required, with cooling, at room temperature or with heating, for example in a temperature range of approximately from -80°C to the boiling temperature of the reaction medium, preferably from approximately 0°C to approximately +150°C, and, if necessary, in a closed vessel, under pressure, under an inert gas atmosphere and/or under anhydrous conditions. Especially advantageous reaction conditions can be found in the Examples.

The reaction time is not critical; a reaction time of from approximately 0.1 to approximately 72 hours, especially from approximately 0.5 to approximately 24 hours, is preferred.

The product is isolated by customary methods, for example by means of filtration, crystallisation, distillation or chromatography, or any suitable combination of such methods.

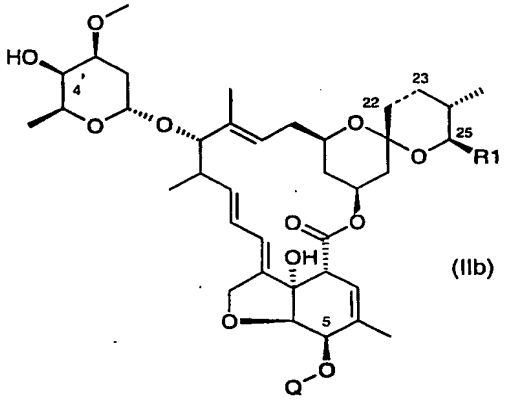
The starting materials mentioned hereinbefore and hereinafter that are used for the preparation of the compounds of formula (I) and, where applicable, their tautomers are known or can be prepared by methods known *per se*, e.g. as indicated below.

The starting materials of formulae



(IIa)

and



(IIb)

wherein the bond between the carbon atoms 22 and 23 may be a single or a double bond and R_1 and Q are as defined above are known to the person skilled in the art (abamectin B1a or 4'-*epi*-abamectin B1a each provided with a protecting group in the 5-position) or can be prepared by methods known *per se*.

Process variant (A):

Examples of solvents and diluents include: aromatic, aliphatic and alicyclic hydrocarbons and halogenated hydrocarbons, such as benzene, toluene, xylene, mesitylene, tetralin, chlorobenzene, dichlorobenzene, bromobenzene, petroleum ether, hexane, cyclohexane, dichloromethane, trichloromethane, tetrachloromethane, dichloroethane, trichloroethene or tetrachloroethene; ethers, such as diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, tert-butyl methyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol dimethyl ether, dimethoxydiethyl ether, tetrahydrofuran or dioxane; esters of carboxylic acids, such as ethyl acetate; amides, such as dimethylformamide, dimethylacetamide or 1-methyl-2-pyrrolidinones; nitriles, such as acetonitrile; sulfoxides, such as dimethyl sulfoxide; or mixtures of the mentioned solvents. Preference is given to amides, such as dimethylformamide and dimethylacetamide, especially dimethylacetamide.

Protecting groups Q in the compounds of formulae (II) and (IV) include: alkyl ether radicals, such as methoxymethyl, methylthiomethyl, tert-butylthiomethyl, benzyloxymethyl, p-

methoxybenzyl, 2-methoxyethoxymethyl, 2,2,2-trichloroethoxymethyl, 2-(trimethylsilyl)ethoxymethyl, tetrahydropyranyl, tetrahydrofuranyl, 1-ethoxyethyl, 1-(2-chloroethoxy)ethyl, 1-methyl-1-methoxyethyl, 1-methyl-1-benzyloxyethyl, trichloroethyl, 2-trimethylsilylethyl, tert-butyl, allyl, p-methoxyphenyl, 2,4-dinitrophenyl, benzyl, p-methoxybenzyl, o-nitrobenzyl, p-nitrobenzyl, triphenylmethyl; trialkylsilyl radicals, such as trimethylsilyl, triethylsilyl, dimethyl-tert-butylsilyl, dimethyl-isopropylsilyl, dimethyl-1,1,2-trimethylpropylsilyl, diethyl-isopropylsilyl, dimethyl-tert-hexylsilyl, but also phenyl-tert-alkylsilyl groups, such as diphenyl-tert-butylsilyl; esters, such as formates, acetates, chloroacetates, dichloroacetates, trichloroacetates, trifluoroacetates, methoxyacetates, phenoxyacetates, pivaloates, benzoates; alkyl carbonates, such as methyl-, 9-fluorenylmethyl-, ethyl-, 2,2,2-trichloroethyl-, 2-(trimethylsilyl)ethyl-, vinyl-, allyl-, benzyl-, p-methoxybenzyl-, o-nitrobenzyl-, p-nitrobenzyl-, but also p-nitrophenyl-carbonate.

Preference is given to trialkylsilyl radicals, such as trimethylsilyl, triethylsilyl, dimethyl-tert-butylsilyl, diphenyl-tert-butylsilyl, esters, such as methoxyacetates and phenoxyacetates, and carbonates, such as 9-fluorenylmethylcarbonates and allylcarbonates. Dimethyl-tert-butylsilyl ether is especially preferred.

The reactions are advantageously carried out in a temperature range of from approximately -70°C to 50°C, preferably at from -10°C to 25°C.

Process variant (B):

Examples of solvents and diluents are the same as those mentioned under Process variant A. In addition, alcohols, such as methanol, ethanol or 2-propanol, and water are suitable.

The reactions are advantageously carried out in a temperature range of approximately from -70°C to 100°C, preferably at from -10°C to 25°C.

There are suitable for the removal of the protecting group Lewis acids, such as hydrochloric acid, methanesulfonic acid, BF_3*OEt_2, HF in pyridine, $Zn(BF_4)_2$*H_2O, p-toluenesulfonic acid, $AlCl_3$, $HgCl_2$; ammonium fluoride, such as tetrabutylammonium fluoride; bases, such as ammonia, trialkylamine or heterocyclic bases; hydrogenolysis with a catalyst, such as palladium-on-carbon; reducing agents, such as sodium borohydride or tributyltin hydride with a catalyst, such as $Pd(PPh_3)_4$, or also zinc with acetic acid.

Preference is given to acids, such as methanesulfonic acid or HF in pyridine; sodium borohydride with Pd(0); bases, such as ammonia, triethylamine or pyridine; especially acids, such as HF in pyridine or methanesulfonic acid.

Process variant (C):

Examples of solvents and diluents are the same as those mentioned under Process variant (A). In addition, alcohols, such as methanol, ethanol or 2-propanol, are suitable. Preference is given to amides, such as dimethylformamide, and nitriles, such as acetonitrile; especially acetonitrile.

The reactions are advantageously carried out in a temperature range of approximately from -10°C to 120°C, preferably at from 20°C to 100°C.

Suitable bases are especially carbonates, such as sodium carbonate, sodium hydrogen carbonate, potassium carbonate, trialkylamines, such as triethylamine, and heterocyclic bases, such as pyridine.

Process variants (D) to (F) are carried out substantially analogously to Process variant (C).

Process variant (G):

Examples of solvents and diluents are the same as those mentioned under Process variant (B).

Ethyl acetate and water are preferred.

The reactions are advantageously carried out in a temperature range of approximately from -10°C to 120°C, preferably at from 20°C to 80°C.

Suitable bases are especially carbonates, such as sodium carbonate, sodium hydrogen carbonate, potassium carbonate, trialkylamines, such as triethylamine, and heterocyclic bases, such as pyridine.

The compounds of formula (I) may be in the form of one of the possible isomers or in the form of a mixture thereof, in the form of pure isomers or in the form of an isomeric mixture, i.e. in the form of a diastereomeric mixture; the invention relates both to the pure isomers and to the diastereomeric mixtures and is to be interpreted accordingly hereinabove and hereinbelow, even if stereochemical details are not mentioned specifically in every case.

The diastereomeric mixtures can be resolved into the pure isomers by known methods, for example by recrystallisation from a solvent, by chromatography, for example high

pressure liquid chromatography (HPLC) on acetylcellulose, with the aid of suitable micro-organisms, by cleavage with specific, immobilised enzymes, or *via* the formation of inclusion compounds, for example using crown ethers, only one isomer being complexed.

Apart from the separation of corresponding mixtures of isomers, pure diastereoisomers can be obtained according to the invention also by generally known methods of stereoselective synthesis, for example by carrying out the process according to the invention using starting materials having correspondingly suitable stereochemistry.

In each case it is advantageous to isolate or synthesise the biologically more active isomer, where the individual components have different biological activity.

The compounds of formula (I) may also be obtained in the form of their hydrates and/or may include other solvents, for example solvents which may have been used for the crystallisation of compounds in solid form.

The invention relates to all those embodiments of the process according to which a compound obtainable as starting material or intermediate at any stage of the process is used as starting material and all or some of the remaining steps are carried out, or in which a starting material is used in the form of a derivative and/or a salt and/or its diastereomers, or, especially, is formed under the reaction conditions. For instance compounds of formula (I) bearing a functional group in its free or protected form can be used as starting materials for the preparation of further compounds of formula (I). For such manipulations methods known to the person skilled in the art can be applied.

In the processes of the present invention it is preferable to use those starting materials and intermediates which result in the compounds of formula (I) that are especially preferred.

The invention relates especially to the preparation processes described in the Examples.

The invention further relates to the compounds of formula (IV) and, where applicable, E/Z isomers, mixtures of E/Z isomers and/or tautomers, in each case in free form or in salt form.

In the area of pest control, the compounds of formula (I) according to the invention are active ingredients exhibiting valuable preventive and/or curative activity with a very advantageous biocidal spectrum and a very broad spectrum, even at low rates of concentration, while being well tolerated by warm-blooded animals, fish and plants. They are, surprisingly, equally suitable for controlling both plant pests and ecto- and endo-parasites in humans and

more especially in productive livestock, domestic animals and pets. They are effective against all or individual development stages of normally sensitive animal pests, but also of resistant animal pests, such as insects and representatives of the order Acarina, nematodes, cestodes and trematodes, while at the same time protecting useful organisms. The insecticidal or acaricidal activity of the active ingredients according to the invention may manifest itself directly, i.e. in the mortality of the pests, which occurs immediately or only after some time, for example during moulting, or indirectly, for example in reduced oviposition and/or hatching rate, good activity corresponding to a mortality of at least 50 to 60 %.

Successful control within the scope of the subject of the invention is possible, in particular, of pests from the orders Lepidoptera, Coleoptera, Orthoptera, Isoptera, Psocoptera, Anoplura, Mallophaga, Thysanoptera, Heteroptera, Homoptera, Hymenoptera, Diptera, Siphonaptera, Thysanura and Acarina, mainly Acarina, Diptera, Thysanoptera, Lepidoptera and Coleoptera. Very especially good control is possible of the following pests:

Abagrotis spp., Abraxas spp., Acantholeucania spp., Acanthoplusia spp., Acarus spp., Acarus siro, Aceria spp., Aceria sheldoni, Acleris spp., Acoloithus spp., Acompsia spp., Acossus spp., Acria spp., Acrobasis spp., Acrocercops spp., Acrolepia spp., Acrolepiopsis spp., Acronicta spp., Acropolitis spp., Actebia spp., Aculus spp., Aculus schlechtendali, Adoxophyes spp., Adoxophyes reticulana, Aedes spp., Aegeria spp., Aethes spp., Agapeta spp., Agonopterix spp., Agriopis spp., Agriotes spp., Agriphila spp., Agrochola spp., Agroperina spp., Alabama ssp., Alabama argillaceae, Agrotis spp., Albuna spp., Alcathoe spp., Alcis spp., Aleimma spp., Aletia spp., Aleurothrixus spp., Aleurothrixus floccosus, Aleyrodes spp., Aleyrodes brassicae, Allophyes spp., Alsophila spp., Amata spp., Amathes spp., Amblyomma spp., Amblyptilia spp., Ammoconia spp., Amorbia spp., Amphion spp., Amphipoea spp., Amphipyra spp., Amyelois spp., Anacamptodes spp., Anagrapha spp., Anarsia spp., Anatrychyntis spp., Anavitrinella spp., Ancylis spp., Andropolia spp., Anhimella spp., Antheraea spp., Antherigona spp., Antherigona soccata, Anthonomus ssp., Anthonomus grandis, Anticarsia spp., Anticarsia gemmatalis, Aonidiella spp., Apamea spp., Aphania spp., Aphelia spp., Aphididae, Aphis spp., Apotomis spp., Aproaerema spp.; Archippus spp., Archips spp., Acromyrmex, Arctia spp., Argas spp., Argolamprotes spp., Argyresthia spp., Argyrogramma spp., Argyroploce spp., Argyrotaenia spp., Arotrophora spp., Ascotis spp., Aspidiotus spp., Aspilapteryx spp., Asthenoptycha spp., Aterpia spp., Athetis spp., Atomaria spp., Atomaria linearis, Atta spp., Atypha spp., Autographa spp., Axylia spp., Bactra spp., Barbara spp., Batrachedra spp., Battaristis spp., Bembecia spp., Bemisia spp., Bemisia tabaci, Bibio spp., Bibio hortulanis, Bisigna spp., Blastesthia spp., Blatta spp., Blatella spp.,

Blepharosis spp., Bleptina spp., Boarmia spp., Bombyx spp., Bomolocha spp., Boophilus spp., Brachmia spp., Bradina spp., Brevipalpus spp., Brithys spp., Bryobia spp., Bryobia praetiosa, Bryotropha spp., Bupalus spp., Busseola spp., Busseola fusca, Cabera spp., Cacoecimorpha spp., Cadra spp., Cadra cautella, Caenurgina spp., Calipitrimerus spp., Callierges spp., Callophpora spp., Callophpora erythrocephala, Calophasia spp., Caloptilia spp., Calybites spp., Capnoptycha spp., Capua spp., Caradrina spp., Caripeta spp., Carmenta spp., Carposina spp., Carposina nipponensis, Catamacta spp., Catelaphris spp., Catoptria spp., Caustoloma spp., Celaena spp., Celypha spp., Cenopis spp., Cephus spp., Ceramica spp., Cerapteryx spp., Ceratitis spp, Ceratophyllus spp., Ceroplaster spp., Chaetocnema spp., Chaetocnema tibialis, Chamaesphecia spp., Charanvca spp., Cheimophila spp., Chersotis spp., Chiasmia spp., Chilo spp., Chionodes spp., Chorioptes spp., Choristoneura spp., Chrysaspidia spp., Chrysodeixis spp., Chrysomya spp., Chrysomphalus spp., Chrysomphalus dictyospermi, Chrysomphalus aonidium, Chrysoteuchia spp., Cilix spp., Cimex spp., Clysia spp., Clysia ambiguella, Clepsis spp., Cnaemidophorus spp., Cnaphalocrocis spp., Cnephasia spp., Coccus spp., Coccus hesperidum, Cochylis spp., Coleophora spp., Colotois spp., Commophila spp., Conistra spp., Conopomorpha spp., Corcyra spp., Cornutiplusia spp., Cosmia spp., Cosmopolites spp., Cosmopterix spp., Cossus spp., Costaeonvexa spp., Crambus spp., Creatonotos spp., Crocidolomia spp., Crocidolomia binotalis, Croesia spp., Crymodes spp., Cryptaspasma spp., Cryptoblabes spp., Cryptocala spp., Cryptophlebia spp., Cryptophlebia leucotreta, Cryptoptila spp., Ctenopseustis spp., Cucullia spp., Curculio spp., Culex spp., Cuterebra spp., Cydia spp., Cydia pomonella, Cymbaiophora spp., Dactylethra spp., Dacus spp., Dadica spp., Damalinea spp., Dasychira spp., Decadarchis spp., Decodes spp., Deilephila spp., Deltodes spp., Dendrolimus spp., Depressaria spp., Dermestes spp., Dermanyssus spp., Dermanyssus gallinae, Diabrotica spp., Diachrysia spp., Diaphania spp., Diarsia spp., Diasemia spp., Diatraea spp., Diceratura spp., Dichomeris spp., Dichrocrocis spp., Dichrorampha spp., Dicycla spp., Dioryctria spp., Diparopsis spp., Diparopsis castanea, Dipleurina spp., Diprion spp., Diprionidae, Discestra spp., Distantiella spp., Distantiella theobroma, Ditula spp., Diurnea spp., Doratopteryx spp., Drepana spp., Drosphila spp., Drosphila melanogaster, Dysauxes spp., Dysdercus spp., Dysstroma spp., Eana spp., Earias spp., Ecclitica spp., Ecdytolopha spp., Ecpyrrhorrhoe spp., Ectomyelois spp., Eetropis spp., Egira spp., Elasmopalpus spp., Emmelia spp., mpoasca spp., Empyreuma spp., Enargia spp., Enarmonia spp., Endopiza spp., Endothenia spp., Endotricha spp., Eoreuma spp., Eotetranychus spp., Eotetranychus carpini, Epagoge spp., Epelis spp., Ephestia spp., Ephestiodes spp., Epiblema spp., Epiehoristodes spp., Epinotia spp.,

Epiphyas spp., Epiplema spp., Epipsestis spp., Epirrhoe spp., Episimus spp., Epitymbia spp., Epllachna spp., Erannis spp., Erastria spp., Eremnus spp., Ereunetis spp., Eriophyes spp., Eriosoma spp., Eriosoma lanigerum, Erythroneura spp., Estigmene spp., Ethmia spp., Etiella spp., Euagrotis spp., Eucosma spp., Euehlaena spp., Euelidia spp., Eueosma spp., Euchistus spp., Eucosmomorpha spp., Eudonia spp., Eufidonia spp., Euhyponomeutoides spp., Eulepitodes spp., Eulia spp., Eulithis spp., Eupithecia spp., Euplexia spp., Eupoecilia spp., Eupoecilia ambiguella, Euproctis spp., Eupsilia spp., Eurhodope spp., Eurois spp., Eurygaster spp., Eurythmia spp., Eustrotia spp., Euxoa spp., Euzophera spp., Evergestis spp., Evippe spp., Exartema spp., Fannia spp., Faronta spp., Feltia spp., Filatima spp., Fishia spp., Frankliniella spp., Fumibotys spp., Gaesa spp., Gasgardia spp., Gastrophilus spp., Gelechia spp., Gilpinia spp., Gilpinia polytoma, Glossina spp., Glyphipterix spp., Glyphodes spp., Gnorimoschemini spp., Gonodonta spp., Gortyna spp., Gracillaria spp., Graphania spp., Grapholita spp., Grapholitha spp., Gravitarmata spp., Gretchena spp., Griselda spp., Gryllotalpa spp., Gynaephora spp., Gypsonoma spp., Hada spp., Haematopinus spp., Halisidota spp., Harpipteryx spp., Harrisina spp., Hedya spp., Helicoverpa spp., Heliophobus spp., Heliothis spp., Hellula spp., Helotropa spp., Hemaris spp., Hercinothrips spp., Hercuiia spp., Hermonassa spp., Heterogenea spp., Holomelina spp., Homadaula spp., Homoeosoma spp., Homogiaea spp., Homohadena spp., Homona spp., Homonopsis spp., Hoplocampa spp., Hoplodrina spp., Hoshinoa spp., Hxalomma spp., Hydraecia spp., Hydriomena spp., Hyles spp., Hyloicus spp., Hypagyrtis spp., Hypatima spp., Hyphantria spp., Hyphantria cunea, Hypocaia spp., Hypocoena spp., Hypodema spp., Hyppobosca spp., Hypsipyla spp., Hyssia spp., Hysterosia spp., Idaea spp., Idia spp., Ipimorpha spp., Isia spp., Isochorista spp., Isophrictis spp., Isopolia spp., Isotrias spp., Ixodes spp., Itame spp., Jodia spp., Jodis spp., Kawabea spp., Keiferia spp., Keiferia lycopersicella, Labdia spp., Lacinipolia spp., Lambdina spp., Lamprothritpa spp., Laodelphax spp., Lasius spp., Laspeyresia spp., Leptinotarsa spp., Leptinotarsa decemlineata, Leptocorisa spp., Leptostales spp., Lecanium spp., Lecanium comi, Lepidosaphes spp., Lepisma spp., Lepisma saccharina , Lesmone spp., Leucania spp., Leucinodes spp., Leucophaea spp., Leucophaea maderae, Leucoptera spp., Leucoptera scitella, Linognathus spp., Liposcelis spp., Lissorhoptrus spp., Lithacodia spp., Lithocolletis spp., Lithomoia spp., Lithophane spp., Lixodessa spp., Lobesia spp., Lobesia botrana, Lobophora spp., Locusta spp., Lomanaltes spp., Lomographa spp., Loxagrotis spp., Loxostege spp., Lucilia spp., Lymantria spp., Lymnaecia spp., Lyonetia spp., Lyriomyza spp., Macdonnoughia spp., Macrauzata spp., Macronoctua spp., Macrosiphus spp., Malacosoma spp., Maliarpha spp., Mamestra spp., Mamestra brassicae,

Manduca spp., Manduca sexta, Marasmia spp., Margaritia spp., Matratinea spp., Matsumuraeses spp., Melanagromyza spp., Melipotes spp., Melissopus spp., Melittia spp., Melolontha spp., Meristis spp., Meritastis spp., Merophyas spp., Mesapamea spp., Mesogona spp., Mesoleuca spp., Metanema spp., Metendothenia spp., Metzneria spp., Micardia spp., Microcorses spp., Microleon spp., Mnesictena spp., Mocis spp., Monima spp., Monochroa spp., Monomorium spp., Monomorium pharaonis, Monopsis spp., Morrisonia spp., Musca spp., Mutuuraia spp., Myelois spp., Mythimna spp., Myzus spp., Naranga spp., Nedra spp., Nemapogon spp., Neodiprion spp., Neosphaleroptera spp., Nephelodes spp., Nephotettix spp., Nezara spp., Nilaparvata spp., Niphonympha spp., Nippoptilia spp., Noctua spp., Nola spp., Notocelia spp., Notodonta spp., Nudaurelia spp., Ochropleura spp., Ocnerostoma spp., Oestrus spp., Olethreutes spp., Oligia spp., Olindia spp., Olygonychus spp., Olygonychus gallinae, Oncocnemis spp., Operophtera spp., Ophisma spp., Opogona spp., Oraesia spp., Orniodoros spp., Orgyia spp., Oria spp., Orseolia spp., Orthodes spp., Orthogonia spp., Orthosia spp., Oryzaephilus spp., Oscinella spp., Oscinella frit, Osminia spp., Ostrinia spp., Ostrinia nubilalis, Otiorhynchus spp., Ourapteryx spp., Pachetra spp., Pachysphinx spp., Pagyda spp., Paleacrita spp., Paliga spp., Palthis spp., Pammene spp., Pandemis spp., Panemeria spp., Panolis spp., Panolis flammea, Panonychus spp., Parargyresthia spp., Paradiarsia spp., Paralobesia spp., Paranthrene spp., Parapandemis spp., Parapediasia spp., Parastichtis spp., Parasyndemis spp., Paratoria spp., Parerommeme spp., Pectinophora spp., Pectinophora gossypiella, Pediculus spp., Pegomyia spp., Pegomyia hyoscyami, Pelochrista spp., Pennisetia spp., Penstemonia spp., Pemphigus spp., Peribatodes spp., Peridroma spp., Perileucoptera spp., Periplaneta spp., Perizoma spp., Petrova spp., Pexicopia spp., Phalonia spp., Phalonidia spp., Phaneta spp., Phlyctaenia spp., Phlyctinus spp., Phorbia spp., Phragmatobia spp., Phricanthes spp., Phthorimaea spp., Phthorimaea operculella, Phyllocnistis spp., Phyllocoptruta spp., Phyllocoptruta oleivora, Phyllonorycter spp., Phyllophila spp., Phylloxera spp., Pieris spp., Pieris rapae, Piesma spp., Planococus spp., Planotortrix spp., Platyedra spp., Platynota spp., Platyptilia spp., Platysenta spp., Plodia spp., Plusia spp., Plutella spp., Plutella xylostella, Podosesia spp., Polia spp., Popillia spp., Polymixis spp., Polyphagotarsonemus spp., Polyphagotarsonemus latus, Prays spp., Prionoxystus spp., Probole spp., Proceras spp., Prochoerodes spp., Proeulia spp., Proschistis spp., Proselena spp., Proserpinus spp., Protagrotis spp., Proteoteras spp., Protobathra spp., Protoschinia spp., Pselnophorus spp., Pseudaletia spp., Pseudanthonomus spp., Pseudaternelia spp., Pseudaulacaspis spp., Pseudexentera spp., Pseudococus spp., Pseudohermenias spp., Pseudoplusia spp., Psoroptes spp., Psylla spp., Psylliodes spp.,

Pterophorus spp., Ptycholoma spp., Pulvinaria spp., Pulvinaria aethiopica, Pyralis spp., Pyrausta spp., Pyrgotis spp., Pyrreferra spp., Pyrrharctia spp., Quadraspidiotus spp., Rancora spp., Raphia spp., Reticultermes spp., Retinia spp., Rhagoletis spp, Rhagoletis pomonella, Rhipicephalus spp., Rhizoglyphus spp., Rhizopertha spp., Rhodnius spp., Rhophalosiphum spp., Rhopobota spp., Rhyacia spp., Rhyacionia spp., Rhynchopacha spp., Rhyzosthenes spp., Rivula spp., Rondotia spp., Rusidrina spp., Rynchaglaea spp., Sabulodes spp., Sahlbergella spp., Sahlbergella singularis, Saissetia spp., Samia spp., Sannina spp., Sanninoidea spp., Saphoideus spp., Sarcoptes spp., Sathrobrota spp., Scarabeidae, Sceliodes spp., Schinia spp., Schistocerca spp., Schizaphis spp., Schizura spp., Schreckensteinia spp., Sciara spp., Scirpophaga spp., Scirthrips auranti, Scoparia spp., Scopula spp., Scotia spp., Scotinophara spp., Scotogramma spp., Scrobipalpa spp., Scrobipalpopsis spp., Semiothisa spp., Sereda spp., Sesamia spp., Sesia spp., Sicya spp., Sideridis spp., Simyra spp., Sineugraphe spp., Sitochroa spp., Sitobion spp., Sitophilus spp., Sitotroga spp., Solenopsis spp., Smerinthus spp., Sophronia spp., Spaelotis spp., Spargaloma spp., Sparganothis spp., Spatalistis spp., Sperchia spp., Sphecia spp., Sphinx spp., Spilonota spp., Spodoptera spp., Spodoptera littoralis, Stagmatophora spp., Staphylinochrous spp., Stathmopoda spp., Stenodes spp., Sterrha spp., Stomoxys spp., Strophedra spp., Sunira spp., Sutyna spp., Swammerdamia spp., Syllomatia spp., Sympistis spp., Synanthedon spp., Synaxis spp., Syncopacma spp., Syndemis spp., Syngrapha spp., Synthomeida spp., Tabanus spp., Taeniarchis spp., Taeniothrips spp., Tannia spp., Tarsonemus spp., Tegulifera spp., Tehama spp., Teleiodes spp., Telorta spp., Tenebrio spp., Tephrina spp., Teratoglaea spp., Terricula spp., Tethea spp., Tetranychus spp., Thalpophila spp., Thaumetopoea spp., Thiodia spp., Thrips spp., Thrips palmi, Thrips tabaci, Thyridopteryx spp., Thyris spp., Tineola spp., Tipula spp., Tortricidia spp., Tortrix spp., Trachea spp., Trialeurodes spp., Trialeurodes vaporariorum, Triatoma spp., Triaxomera spp., Tribolium spp., Tricodectes spp., Trichoplusia spp., Trichoplusia ni, Trichoptilus spp., Trioza spp., Trioza erytreae, Triphaenia spp., Triphosa spp., Trogoderma spp., Tyria spp., Udea spp., Unaspis spp., Unaspis citri, Utetheisa spp., Valeriodes spp., Vespa spp., Vespamima spp., Vitacea spp., Vitula spp., Witlesia spp., Xanthia spp., Xanthorhoe spp., Xanthotype spp., Xenomicta spp., Xenopsylla spp., Xenopsylla cheopsis, Xestia spp., Xylena spp., Xylomyges spp., Xyrosaris spp., Yponomeuta spp., Ypsolopha spp., Zale spp., Zanclognathus spp., Zeiraphera spp., Zenodoxus spp., Zeuzera spp., Zygaena spp.,

It is also possible to control pests of the class Nematoda using the compounds according to the invention. Such pests include, for example,

root knot nematodes, cyst-forming nematodes and also stem and leaf nematodes;

especially of Heterodera spp., e.g. Heterodera schachtii, Heterodora avenae and Heterodora trifolii; Globodera spp., e.g. Globodera rostochiensis; Meloidogyne spp., e.g. Meloidogyne incognita and Meloidogyne javanica; Radopholus spp., e.g. Radopholus similis; Pratylenchus, e.g. Pratylenchus neglectans and Pratylenchus penetrans; Tylenchulus, e.g. Tylenchulus semipenetrans; Longidorus, Trichodorus, Xiphinema, Ditylenchus, Apheenchoides and Anguina; especially Meloidogyne, e.g. Meloidogyne incognita, and Heterodera, e.g. Heterodera glycines.

An especially important aspect of the present invention is the use of the compounds of formula (I) according to the invention in the protection of plants against parasitic feeding pests.

The action of the compounds according to the invention and the compositions comprising them against animal pests can be significantly broadened and adapted to the given circumstances by the addition of other insecticides, acaricides or nematicides. Suitable additives include, for example, representatives of the following classes of active ingredient: organophosphorus compounds, nitrophenols and derivatives, formamidines, ureas, carbamates, pyrethroids, chlorinated hydrocarbons, neonicotinoids and Bacillus thuringiensis preparations.

Examples of especially suitable mixing partners include: azamethiphos; chlorfenvinphos; cypermethrin, cypermethrin high-cis; cyromazine; diafenthiuron; diazinon; dichlorvos; dicrotophos; dicyclanil; fenoxycarb; fluazuron; furathiocarb; isazofos; iodfenphos; kinoprene; lufenuron; methacriphos; methidathion; monocrotophos; phosphamidon; profenofos; diofenolan; a compound obtainable from the Bacillus thuringiensis strain GC91 or from strain NCTC11821; pymetrozine; bromopropylate; methoprene; disulfoton; quinalphos; taufluvalinate; thiocyclam; thiometon; aldicarb; azinphos-methyl; benfuracarb; bifenthrin; buprofezin; carbofuran; dibutylaminothio; cartap; chlorfluazuron; chlorpyrifos; clothianidin; cyfluthrin; lambda-cyhalothrin; alpha-cypermethrin; zeta-cypermethrin; deltamethrin; diflubenzuron; endosulfan; ethiofencarb; fenitrothion; fenobucarb; fenvalerate; formothion; methiocarb; heptenophos; imidacloprid; isoprocarb; methamidophos; methomyl; mevinphos; parathion; parathion-methyl; phosalone; pirimicarb; propoxur; teflubenzuron; terbufos; triazamate; fenobucarb; tebufenozide; fipronil; beta-cyfluthrin; silafluofen; fenpyroximate; pyridaben; fenazaquin; pyriproxyfen; pyrimidifen; nitenpyram; acetamiprid; emamectin; emamectin-benzoate; spinosad; a plant extract that is active against insects; a preparation

that comprises nematodes and is active against insects; a preparation obtainable from Bacillus subtilis; a preparation that comprises fungi and is active against insects; a preparation that comprises viruses and is active against insects; chlorfenapyr; acephate; acrinathrin; alanycarb; alphamethrin; amitraz; AZ 60541; azinphos A; azinphos M; azocyclotin; bendiocarb; bensultap; beta-cyfluthrin; BPMC; brofenprox; bromophos A; bufencarb; butocarboxin; butylpyridaben; cadusafos; carbaryl; carbophenothion; chloethocarb; chlorethoxyfos; chlormephos; cis-resmethrin; clocythrin; clofentezine; cyanophos; cycloprothrin; cyhexatin; demeton M; demeton S; demeton-S-methyl; dichlofenthion; dicliphos; diethion; dimethoate; dimethylvinphos; dioxathion; edifenphos; esfenvalerate; ethion; ethofenprox; ethoprophos; etrimphos; fenamiphos; fenbutatin oxide; fenothiocarb; fenpropathrin; fenpyrad; fenthion; fluazinam; flucycloxuron; flucythrinate; flufenoxuron; flufenprox; fonophos; fosthiazate; fubfenprox; HCH; hexaflumuron; hexythiazox; IKI-220; iprobenfos; isofenphos; isoxathion; ivermectin; malathion; mecarbam; mesulfenphos; metaldehyde; metolcarb; milbemectin; moxidectin; naled; NC 184; nithiazine; omethoate; oxamyl; oxydemethon M; oxydeprofos; permethrin; phenthoate; phorate; phosmet; phoxim; pirimiphos M; pirimiphos E; promecarb; propaphos; prothiofos; prothoate; pyrachlophos; pyradaphenthion; pyresmethrin; pyrethrum; tebufenozide; salithion; sebufos; sulfotep; sulprofos; tebufenpyrad; tebupirimphos; tefluthrin; temephos; terbam; tetrachlorvinphos; thiacloprid; thiafenox; thiamethoxam; thiodicarb; thiofanox; thionazin; thuringiensin; tralomethrin; triarathene; triazophos; triazuron; trichlorfon; triflumuron; trimethacarb; vamidothion; xylylcarb; YI 5301/5302; zetamethrin; DPX-MP062 — indoxacarb; methoxyfenozide; bifenazate; XMC (3,5-xylyl methylcarbamate); or the fungus pathogen Metarhizium anisopliae.

The compounds according to the invention can be used to control, i.e. to inhibit or destroy, pests of the mentioned type occurring on plants, especially on useful plants and ornamentals in agriculture, in horticulture and in forestry, or on parts of such plants, such as the fruits, blossoms, leaves, stems, tubers or roots, while in some cases plant parts that grow later are still protected against those pests.

Target crops include especially cereals, such as wheat, barley, rye, oats, rice, maize and sorghum; beet, such as sugar beet and fodder beet; fruit, e.g. pomes, stone fruit and soft fruit, such as apples, pears, plums, peaches, almonds, cherries and berries, e.g. strawberries, raspberries and blackberries; leguminous plants, such as beans, lentils, peas and soybeans; oil plants, such as rape, mustard, poppy, olives, sunflowers, coconut, castor oil, cocoa and groundnuts; cucurbitaceae, such as marrows, cucumbers and melons; fibre

plants, such as cotton, flax, hemp and jute; citrus fruits, such as oranges, lemons, grapefruit and mandarins; vegetables, such as spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes and paprika; lauraceae, such as avocado, cinnamon and camphor; and tobacco, nuts, coffee, aubergines, sugar cane, tea, pepper, vines, hops, bananas, natural rubber plants and ornamentals.

Further areas of use of the compounds according to the invention are the protection of stored goods and storerooms and the protection of raw materials, and also in the hygiene sector, especially the protection of domestic animals and productive livestock against pests of the mentioned type, more especially the protection of domestic animals, especially cats and dogs, from infestation by fleas, ticks and nematodes.

The invention therefore relates also to pesticidal compositions, such as emulsifiable concentrates, suspension concentrates, directly sprayable or dilutable solutions, spreadable pastes, dilute emulsions, wettable powders, soluble powders, dispersible powders, wettable powders, dusts, granules and encapsulations of polymer substances, that comprise at least one of the compounds according to the invention, the choice of formulation being made in accordance with the intended objectives and the prevailing circumstances.

The active ingredient is used in those compositions in pure form, a solid active ingredient, for example, in a specific particle size, or preferably together with at least one of the adjuvants customary in formulation technology, such as extenders, e.g. solvents or solid carriers, or surface-active compounds (surfactants). In the area of parasite control in humans, domestic animals, productive livestock and pets it will be self-evident that only physiologically tolerable additives are used.

Solvents are, for example: non-hydrogenated or partly hydrogenated aromatic hydrocarbons, preferably fractions C_8 to C_{12} of alkylbenzenes, such as xylene mixtures, alkylated naphthalenes or tetrahydronaphthalene, aliphatic or cycloaliphatic hydrocarbons, such as paraffins or cyclohexane, alcohols, such as ethanol, propanol or butanol, glycols and ethers and esters thereof, such as propylene glycol, dipropylene glycol ether, ethylene glycol or ethylene glycol monomethyl or -ethyl ether, ketones, such as cyclohexanone, isophorone or diacetone alcohol, strongly polar solvents, such as N-methylpyrrolid-2-one, dimethyl sulfoxide or N,N-dimethylformamide, water, non-epoxidized or epoxidized plant oils, such as non-epoxidized or epoxidized rapeseed, castor, coconut or soya oil, and silicone oils.

The solid carriers used, for example for dusts and dispersible powders, are as a rule natural rock powders, such as calcite, talc, kaolin, montmorillonite or attapulgite. Highly

disperse silicic acids or highly disperse absorbent polymers can also be added to improve the physical properties. Granular adsorptive granule carriers are porous types, such as pumice, crushed brick, sepiolite or bentonite, and non-sorbent carrier materials are calcite or sand. A large number of granular materials of inorganic or organic nature can furthermore be used, in particular dolomite or comminuted plant residues.

Surface-active compounds are, depending on the nature of the active compound to be formulated, nonionic, cationic and/or anionic surfactants or surfactant mixtures with good emulsifying, dispersing and wetting properties. The surfactants listed below are to be regarded only as examples; many other surfactants which are customary in formulation technology and are suitable according to the invention are described in the relevant literature.

Nonionic surfactants are, in particular, polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, saturated or unsaturated fatty acids and alkylphenols, which can contain 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon radical and 6 to 18 carbon atoms in the alkyl radical of the alkylphenols. Substances which are furthermore suitable are water-soluble polyethylene oxide adducts, containing 20 to 250 ethylene glycol ether and 10 to 100 propylene glycol ether groups, on propylene glycol, ethylene diaminopolypropylene glycol and alkyl polypropylene glycol having 1 to 10 carbon atoms in the alkyl chain. The compounds mentioned usually contain 1 to 5 ethylene glycol units per propylene glycol unit. Examples are nonylphenol-polyethoxyethanols, castor oil polyglycol ethers, polypropylene-polyethylene oxide adducts, tributylphenoxypolyethoxyethanol, polyethylene glycol and octylphenoxypolyethoxyethanol. Other substances are fatty acid esters of polyoxyethylene sorbitan, such as polyoxyethylene sorbitan trioleate.

The cationic surfactants are, in particular, quaternary ammonium salts which contain, as substituents, at least one alkyl radical having 8 to 22 C atoms and, as further substituents, lower, non-halogenated or halogenated alkyl, benzyl or lower hydroxyalkyl radicals. The salts are preferably in the form of halides, methyl-sulfates or ethyl-sulfates. Examples are stearyl-trimethyl-ammonium chloride and benzyl-di-(2-chloroethyl)-ethyl-ammonium bromide.

Suitable anionic surfactants can be both water-soluble soaps and water-soluble synthetic surface-active compounds. Suitable soaps are the alkali metal, alkaline earth metal and substituted or unsubstituted ammonium salts of higher fatty acids (C_{10}-C_{22}), such as the sodium or potassium salts of oleic or stearic acid, or of naturally occurring fatty acid

mixtures, which can be obtained, for example, from coconut oil or tall oil; and furthermore also the fatty acid methyl-taurine salts. However, synthetic surfactants are more frequently used, in particular fatty sulfonates, fatty sulfates, sulfonated benzimidazole derivatives or alkylarylsulfonates. The fatty sulfonates and sulfates are as a rule in the form of alkali metal, alkaline earth metal or substituted or unsubstituted ammonium salts and in general have an alkyl radical of 8 to 22 C atoms, alkyl also including the alkyl moiety of acyl radicals; examples are the sodium or calcium salt of ligninsulfonic acid, of dodecylsulfuric acid ester or of a fatty alcohol sulfate mixture prepared from naturally occurring fatty acids. These also include the salts of sulfuric acid esters and sulfonic acids of fatty alcohol-ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulfonic acid groups and a fatty acid radical having about 8 to 22 C atoms. Alkylarylsulfonates are, for example, the sodium, calcium or triethanolammonium salts of dodecylbenzenesulfonic acid, of dibutylnaphthalenesulfonic acid or of a naphthalenesulfonic acid-formaldehyde condensation product. Corresponding phosphates, such as salts of the phosphoric acid ester of a p-nonylphenol-(4-14)-ethylene oxide adduct or phospholipids, can further also be used.

The compositions as a rule comprise 0.1 to 99 %, in particular 0.1 to 95 %, of active compound and 1 to 99.9 %, in particular 5 to 99.9 %, of - at least - one solid or liquid auxiliary, it being possible as a rule for 0 to 25 %, in particular 0.1 to 20 %, of the composition to be surfactants (% is in each case per cent by weight). While concentrated compositions are more preferred as commercial goods, the end user as a rule uses dilute compositions which comprise considerably lower concentrations of active compound. Preferred compositions are composed, in particular, as follows (% = per cent by weight):

Emulsifiable concentrates:

active ingredient:	1 to 90%, preferably 5 to 20%
surfactant:	1 to 30%, preferably 10 to 20%
solvent:	5 to 98%, preferably 70 to 85%

Dusts:

active ingredient:	0.1 to 10%, preferably 0.1 to 1%
solid carrier:	99.9 to 90%, preferably 99.9 to 99%

Suspension concentrates:	
active ingredient:	5 to 75%, preferably 10 to 50%
water:	94 to 24%, preferably 88 to 30%
surfactant:	1 to 40%, preferably 2 to 30%
Wettable powders:	
active ingredient:	0.5 to 90%, preferably 1 to 80%
surfactant:	0.5 to 20%, preferably 1 to 15%
solid carrier:	5 to 99%, preferably 15 to 98%
Granules:	
active ingredient:	0.5 to 30%, preferably 3 to 15%
solid carrier:	99.5 to 70%, preferably 97 to 85%

The compositions according to the invention may also comprise further solid or liquid adjuvants, such as stabilisers, e.g. vegetable oils or epoxidised vegetable oils (e.g. epoxidised coconut oil, rapeseed oil or soybean oil), antifoams, e.g. silicone oil, preservatives, viscosity regulators, binders and/or tackifiers as well as fertilisers or other active ingredients for obtaining special effects, e.g. acaricides, bactericides, fungicides, nematicides, molluscicides or selective herbicides.

The crop protection products according to the invention are prepared in known manner, in the absence of adjuvants, e.g. by grinding, sieving and/or compressing a solid active ingredient or mixture of active ingredients, for example to a certain particle size, and in the presence of at least one adjuvant, for example by intimately mixing and/or grinding the active ingredient or mixture of active ingredients with the adjuvant(s). The invention relates likewise to those processes for the preparation of the compositions according to the invention and to the use of the compounds of formula (I) in the preparation of those compositions.

The invention relates also to the methods of application of the crop protection products, i.e. the methods of controlling pests of the mentioned type, such as spraying, atomising, dusting, coating, dressing, scattering or pouring, which are selected in accordance with the intended objectives and the prevailing circumstances, and to the use of the compositions for controlling pests of the mentioned type. Typical rates of concentration are from 0.1 to 1000 ppm, preferably from 0.1 to 500 ppm, of active ingredient. The rates of application per hectare are generally from 1 to 2000 g of active ingredient per hectare, especially from 10 to 1000 g/ha, preferably from 20 to 600 g/ha.

A preferred method of application in the area of crop protection is application to the foliage of the plants (foliar application), the frequency and the rate of application being dependent upon the risk of infestation by the pest in question. However, the active ingredient can also penetrate the plants through the roots (systemic action) when the locus of the plants is impregnated with a liquid formulation or when the active ingredient is incorporated in solid form into the locus of the plants, for example into the soil, e.g. in granular form (soil application). In the case of paddy rice crops, such granules may be applied in metered amounts to the flooded rice field.

The crop protection products according to the invention are also suitable for protecting plant propagation material, e.g. seed, such as fruits, tubers or grains, or plant cuttings, against animal pests. The propagation material can be treated with the composition before planting: seed, for example, can be dressed before being sown. The active ingredients according to the invention can also be applied to grains (coating), either by impregnating the seeds in a liquid formulation or by coating them with a solid formulation. The composition can also be applied to the planting site when the propagation material is being planted, for example to the seed furrow during sowing. The invention relates also to such methods of treating plant propagation material and to the plant propagation material so treated.

The following Examples serve to illustrate the invention. They do not limit the invention. Temperatures are given in degrees Celsius; mixing ratios of solvents are given in parts by volume.

Preparation Examples

In the following Examples, the preparation of avermectin B1 derivatives (mixtures of avermectin B1a and B1b derivative) is described. The B1b derivative generally represents about only from 5 to 10 % by weight of the mixtures and, for that reason, usually only the bands of the B1a derivative can be detected in the NMR spectrum.

Since the compounds are in most cases in the form of mixtures of the avermectin B1a and B1b derivative, characterisation by means of the customary physical data such as melting point or refractive index is of little use. For that reason, the compounds are characterised by reference to the retention times determined in analysis by means of HPLC (high-resolution liquid chromatography). The term "B1a" in the physical data on the Preparation Examples refers to the main component, wherein R_1 is sec-butyl. "B1b" represents the secondary component, wherein R_1 is isopropyl. In the case of the compounds for which a retention time is given only for the B1a derivative, it is not possible to determine the retention

time for the B1b component owing to the small proportion of B1b derivative. Allocation of the correct structures of the B1a and B1b components is carried out by mass spectrometry.

The following method is used for the HPLC analysis:

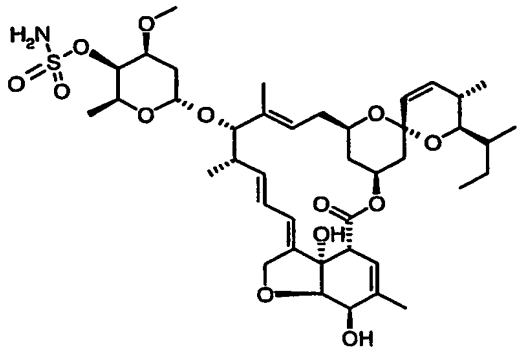
HPLC gradient conditions			
solvent A:	0.01% trifluoroacetic acid in H_2O		
solvent B:	0.01% trifluoroacetic acid in CH_3CN		
time [min]	A [%]	B [%]	flow rate [µl/min]
0	80	20	500
0.1	50	50	500
10	5	95	500
15	0	100	500
17	0	100	500
17.1	80	20	500
22	80	20	500
column:	YMC-Pack ODS-AQ		
column length:	125 mm		
column internal diameter:	2 mm		
temperature:	40 °C		

The YMC-Pack ODS-AQ column used for chromatography of the compounds is produced by YMC, Alte Raesfelderstrasse 6, 46514 Schermbeck, Germany.

The abbreviations used in the physical data information have the following meanings:

LCMS: liquid chromatography mass spectrometry; t_{RT}: retention time in minutes; M+H: mass peak plus H; M+Na: mass peak plus Na. TBDMS in the Examples represents the radical -Si(CH_3)$_2$(tert-butyl). Mixing ratios of solvents are given in parts by volume. "Ether" is understood to mean diethyl ether.

Example P.1: Preparation of 4'-*(R)*-O-sulfamoyloxy-avermectin B1 monosaccharide of the formula

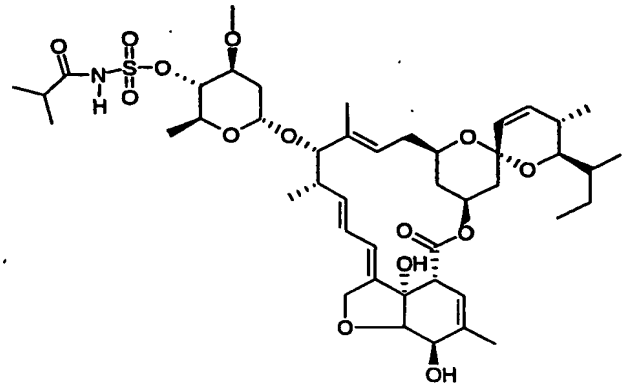


Preparation of sulfamoyl chloride ($ClSO_2NH_2$): 15.5 ml of formic acid are added dropwise at -10°C to 35 ml of chlorosulfonyl isocyanate and the temperature is maintained below +10°C by cooling with ice. At the end of the addition, stirring is continued at room temperature until the evolution of gas ceases. The mixture is taken up in benzene, filtered, and concentrated by evaporation *in vacuo*, yielding the desired sulfamoyl chloride.

Step A: 3.51 g of sulfamoyl chloride are added in portions at -10°C to a solution of 15 g of 5-O-TBDMS-avermectin B_1 monosaccharide in 90 ml of dimethylacetamide under argon. The mixture is allowed to warm to room temperature and is stirred for a further hour. The mixture is poured onto saturated aqueous NaCl solution, extracted twice with tert-butyl methyl ether, dried over Na_2SO_4 and concentrated by evaporation, yielding the desired intermediate 5-O-TBDMS-4'-O-sulfamoyloxy-avermectin B_1 monosaccharide.

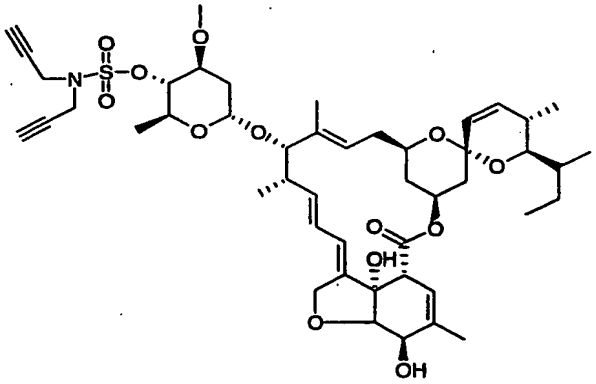
Step B: The crude product from Step A is dissolved in 75 ml of methanol. Then, at -5°C, 1.5 ml of methanesulfonic acid in 75 ml of methanol are added dropwise in the course of one hour. The mixture is allowed to warm to room temperature and is left to react for four hours. The solution is poured onto saturated aqueous $NaHCO_3$ solution, concentrated by evaporation *in vacuo*, and extracted twice with tert-butyl methyl ether. Washing with saturated aqueous NaCl solution, drying over Na_2SO_4 and concentration by evaporation yield the crude product. Flash column chromatography on silica gel in CH_2Cl_2/ethyl acetate (9:1) yields the desired product in the form of a colourless foam.

Example P.2: Preparation of 4'-Isobutyroylaminosulfonyloxy- avermectin B1 monosaccharide of the formula



A mixture of 490 mg of 4'-sulfamoyloxy-5-O-t-butyldimethylsilyl-avermectin B1 monosaccharide, 0.26 ml of isobutyryl chloride and 0.41 ml of pyridine in 10 ml of dichloromethane is stirred overnight at 25 °C. The mixture is filtered on silica gel and evaporated to dryness. The crude product is dissolved in 12 ml of tetrahydrofuran and a solution of 2.5 mL HF-Pyridine complex is added. The mixture is stirred overnight at room temperature. The mixture is poured onto a saturated solution of sodium hydrogen carbonate and extracted three times with ethyl acetate and the organic phases are combined and dried over Na_2SO_4. The desired product is isolated from the crude mixture by column chromatography on silicagel in hexane/ ethyl acetate (1:1).

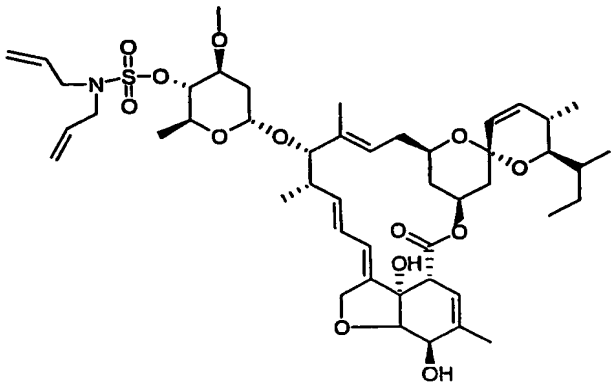
Example P.3: Preparation of 4'-*(S)*-dipropargylaminosulfonyloxy- avermectin B1 monosaccharide of the formula



A mixture of 490 mg of 4'-sulfamoyloxy -avermectin B monosaccharide, 230 mg of potassium carbonate and 0.15 ml of propargyl bromide in 10 ml of acetonitrile is stirred at 50°C for 3 hours. The solution is poured onto water, extracted with ethyl acetate and dried over Na_2SO_4. The desired product is isolated from the crude mixture by column chromatography on silica gel in hexane/ ethyl acetate (1:4).

Example P.4: Preparation of 4'-*(S)*-Diallylaminosulfonyloxy- avermectin B1

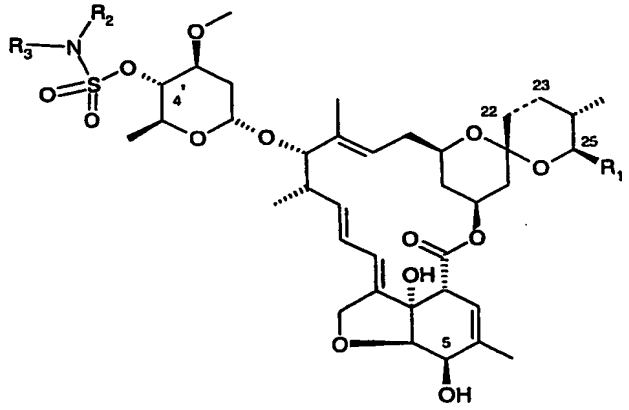
monosaccharide



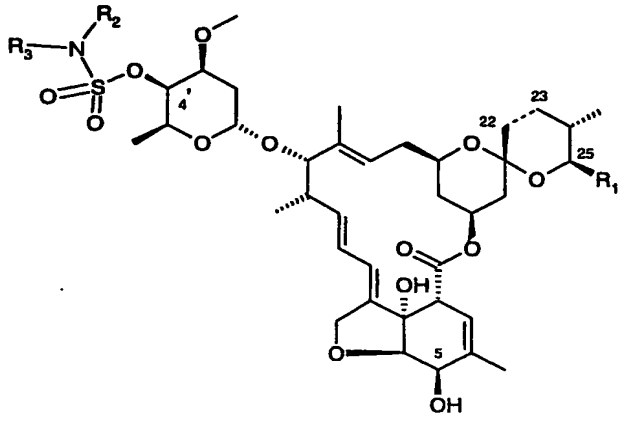
A mixture of 440 mg of 4'-sulfamoyloxy -avermectin B monosaccharide, 280 mg of potassium carbonate and 0.2 ml of propargyl bromide in 10 ml of acetonitrile is stirred at room temperature overnight and then refluxed for 2 hours. The solution is poured onto a saturated solution of sodium hydrogen-carbonate, extracted with ethyl acetate and dried over Na_2SO_4. The desired product is isolated from the crude mixture by column chromatography on silicagel in hexane/ ethyl acetate (1:1).

The compounds listed in Table A and in Tables 1 to 36 can also be prepared analogously to the above Preparation Examples.

Table A: Compounds of formula



(Ia), or of formula



(Ib)

wherein R_1 is sec-butyl (B1a) or isopropyl (B1b) and the bond between carbon atoms 22 and 23 is a double bond;

No.	Formula	R_2	R_3	retention time (min.)	
				B_{1a}	B_{1b}
A.1	(Ia)	H	H	8.11	-
A.2	(Ia)	C(O)Me	H	7.99	7.47
A.3	(Ia)	$C(O)CH_2OCH_3$	H	8.69	-
A.4	(Ia)	C(O)-i-C_3H_7	H	8.96	8.32
A.5	(Ia)	$C(O)CH_2OC_6H_5$	H	9.77	-
A.6	(Ia)	C(O)-i-C_4H_9	H	9.39	8.75
A.7	(Ia)	$C(O)C_6H_5$	H	9.28	-
A.8	(Ia)	Propargyl	H		
A.9	(Ib)	Allyl	H	5.35	-
A.10	(Ia)	$-CH_2CH_2CH_2CH_2-$			
A.11	(Ia)	Propargyl	propargyl	10.83	-
A.12	(Ia)	Allyl	allyl	11.63	10.93
A.13	(Ia)	$-C(=O)C_2H_5$	H	8.4	-
A.14	(Ia)	$-CH_2OCH_2CH_2OCH_3$	$-CH_2OCH_2CH_2OCH_3$		
A.15	(Ia)	$-CH_2OCH_2CH_2OCH_3$	H		
A.16	(Ib)	H	H	6.99	-
A.17	(Ib)	$C(O)CH_2OCH_3$	H	7.79	-
A.18	(Ib)	C(O)-i-C_3H_7	H	8.16	-
A.19	(Ib)	C(O)-I-C_4H_9	H	9.6	-
A.20	(Ib)	C(O)Me	H	7.85	-
A.21	(Ib)	$C(O)C_6H_5$	H	9.45	10.66
A.22	(Ib)	Propargyl	propargyl	9.89	-
A.23	(Ib)	Allyl	allyl	6.72	-

No.	Formula	R_2	R_3	retention time (min.)	
				B_{1a}	B_{1b}
A.25	(Ib)	Propargyl	H		
A.26	(Ib)	Allyl	H		
A.27	(Ib)	$-C(=O)C_2H_5$	H		
A.28	(Ib)	$-CH_2OCH_2CH_2OCH_3$	$-CH_2OCH_2CH_2OCH_3$		
A.29	(Ib)	$-CH_2OCH_2CH_2OCH_3$	H		

Table B: Compounds of formula (I):

No.	R_2
B.1	isopropyl
B.2	propyl
B.3	n-butyl
B.4	sec-butyl
B.5	isobutyl
B.6	tert-butyl
B.7	$CH(CH_3)CH(CH_3)_2$
B.8	$CH(CH_2CH_3)CH_2Cl$
B.9	$CH(CH_3)CH_2OCH_3$
B.10	2-chloro-propyl
B.11	3-chloro-propyl
B.12	2-chloro-ethyl
B.13	$CH_2CH_2OCH_3$
B.14	2-fluoro-ethyl
B.15	2-(morpholine-4-yl)ethyl
B.16	2-(pyrrolidine-1-yl)ethyl
B.17	cyclopropyl
B.18	cyclobutyl
B.19	cyclopentyl
B.20	cyclohexyl
B.21	bis(trifluoromethyl)methyl
B.22	benzyl
B.23	2-methylallyl
B.24	3-methylallyl
B.25	$CH_2C(O)OCH_3$
B.26	$CH_2CH_2C(O)OCH_3$
B.27	2-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)ethyl
B.28	2-aminoethyl
B.29	2-methylaminoethyl
B.30	2-dimethylaminoethyl
B.31	$CH_2CH_2OC_2H_5$

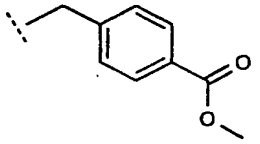
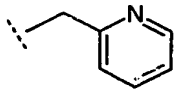
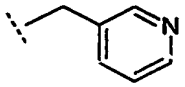
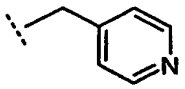
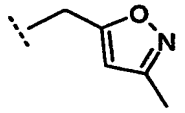
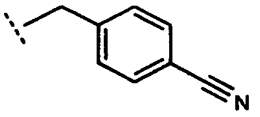
No.	R_2
B.32	$CH_2CH_2OCH_2CH_2OCH_3$
B.33	3-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)propyl
B.34	4-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-butyl
B.35	CH_2CONH_2
B.36	CH_2COOH
B.37	(2-fluorophenyl)methyl
B.38	(3-fluorophenyl)methyl
B.39	(2,6-difluorophenyl)methyl
B.40	(4-fluorophenyl)methyl
B.41	(4-trifluoromethylphenyl)methyl
B.42	
B.43	(4-trifluoromethoxyphenyl)methyl
B.44	(4-difluoromethylphenyl)methyl
B.45	
B.46	
B.47	
B.48	
B.49	
B.50	(4-methoxyphenyl)methyl
B.51	phenyl
B.52	4-chlorophenyl
B.53	Pyrid-3-yl
B.54	2-chloropyrid-5-yl

Table 1: A compound of formula (Ia) wherein R_1 is sec-butyl (B1a) or isopropyl (B1b), R_3 is hydrogen, the bond between carbon atoms 22 and 23 is a double bond and R_2 corresponds to one of the radicals of Table B listed under B.1 to B.54.

Table 2: A compound of formula (Ia) wherein R_1 is sec-butyl (B1a) or isopropyl (B1b), R_3 is hydrogen, the bond between carbon atoms 22 and 23 is a single bond and R_2 corresponds to one of the radicals of Table B listed under B.1 to B.54.

Table 3: A compound of formula (Ib) wherein R_1 is sec-butyl (B1a) or isopropyl (B1b), R_3 is hydrogen, the bond between carbon atoms 22 and 23 is a double bond and R_2 corresponds to one of the radicals of Table B listed under B.1 to B.54.

Table 4: A compound of formula (Ib) wherein R_1 is sec-butyl (B1a) or isopropyl (B1b), R_3 is hydrogen, the bond between carbon atoms 22 and 23 is a single bond and R_2 corresponds to one of the radicals of Table B listed under B.1 to B.54.

Table 5: A compound of formula (Ia) wherein R_1 is cyclohexyl, R_3 is hydrogen, the bond between carbon atoms 22 and 23 is a double bond and R_2 corresponds to one of the radicals of Table B listed under B.1 to B.54.

Table 6: A compound of formula (Ia) wherein R_1 is cyclohexyl, R_3 is hydrogen, the bond between carbon atoms 22 and 23 is a single bond and R_2 corresponds to one of the radicals of Table B listed under B.1 to B.54.

Table 7: A compound of formula (Ib) wherein R_1 is cyclohexyl, R_3 is hydrogen, the bond between carbon atoms 22 and 23 is a double bond and R_2 corresponds to one of the radicals of Table B listed under B.1 to B.54.

Table 8: A compound of formula (Ib) wherein R_1 is cyclohexyl, R_3 is hydrogen, the bond between carbon atoms 22 and 23 is a single bond and R_2 corresponds to one of the radicals of Table B listed under B.1 to B.54.

Table 9: A compound of formula (Ia) wherein R_1 is 1-methyl-butyl, R_3 is hydrogen, the bond between carbon atoms 22 and 23 is a double bond and R_2 corresponds to one of the radicals of Table B listed under B.1 to B.54.

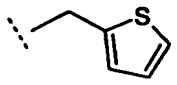
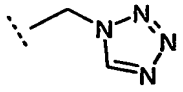
Table 10: A compound of formula (Ia) wherein R_1 is 1-methyl-butyl, R_3 is hydrogen, the bond between carbon atoms 22 and 23 is a single bond and R_2 corresponds to one of the radicals of Table B listed under B.1 to B.54.

Table 11: A compound of formula (Ib) wherein R_1 is 1-methyl-butyl, R_3 is hydrogen, the bond between carbon atoms 22 and 23 is a double bond and R_2 corresponds to one of the radicals of Table B listed under B.1 to B.54.

Table 12: A compound of formula (Ib) wherein R_1 is 1-methyl-butyl, R_3 is hydrogen, the bond

between carbon atoms 22 and 23 is a single bond and R_2 corresponds to one of the radicals of Table B listed under B.1 to B.54.

Table C: Compounds of formula (I)

No.	R_4
C.001	Isopropyl
C.002	Propyl
C.003	n-butyl
C.004	sec-butyl
C.005	Isobutyl
C.006	tert-butyl
C.007	methyl
C.008	ethyl
C.009	vinyl
C.010	2-chloro-propyl
C.011	3-chloro-propyl
C.012	2-chloro-ethyl
C.013	$CH_2CH_2OCH_3$
C.014	allyl
C.015	CH_2OCH_3
C.016	CH_2Ophenyl
C.017	cyclopropyl
C.018	cyclopentyl
C.019	cyclohexyl
C.020	$CH_2CH_2NH_2$
C.021	benzyl
C.022	fluoromethyl
C.023	difluoromethyl
C.024	
C.025	
C.026	$CH_2OCH_2CH_2OCH_3$
C.027	OCH_3
C.028	OCH_2CH_3
C.029	O-allyl

No.	R_4
C.030	OCH_2CH_2OH
C.031	NH_2
C.032	$NHCH_3$
C.033	$N(CH_3)$
C.034	Benzyl
C.035	phenyl
C.036	4-chlorophenyl
C.037	pyrid-3-yl
C.038	2-chloropyrid-5-yl

Table 13: A compound of formula (Ia) wherein R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between carbon atoms 22 and 23 is a double bond, R_2 is $C(=O)R_4$ and R_3 is hydrogen, and R_4 corresponds to one of the radicals of Table C listed under C.1 to C.038.

Table 14: A compound of formula (Ib) wherein R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between carbon atoms 22 and 23 is a double bond, R_2 is $-C(=O)R_4$ and R_3 is hydrogen, and R_4 corresponds to one of the radicals of Table C listed under C.1 to C.038.

Table 15: A compound of formula (Ia) wherein R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between carbon atoms 22 and 23 is a single bond, R_2 is $C(=O)R_4$ and R_3 is hydrogen, and R_4 corresponds to one of the radicals of Table C listed under C.1 to C.038.

Table 16: A compound of formula (Ib) wherein R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between carbon atoms 22 and 23 is a single bond, R_2 is $-C(=O)R_4$ and R_3 is hydrogen, and R_4 corresponds to one of the radicals of Table C listed under C.1 to C.038.

Table 17: A compound of formula (Ia) wherein R_1 is cyclohexyl, the bond between carbon atoms 22 and 23 is a double bond, R_2 is $C(=O)R_4$ and R_3 is hydrogen, and R_4 corresponds to one of the radicals of Table C listed under C.1 to C.038.

Table 18: A compound of formula (Ib) wherein R_1 is cyclohexyl, the bond between carbon atoms 22 and 23 is a double bond, R_2 is $-C(=O)R_4$ and R_3 is hydrogen, and R_4 corresponds to one of the radicals of Table C listed under C.1 to C.038.

Table 19: A compound of formula (Ia) wherein R_1 is cyclohexyl, the bond between carbon atoms 22 and 23 is a single bond, R_2 is $C(=O)R_4$ and R_3 is hydrogen, and R_4 corresponds to one of the radicals of Table C listed under C.1 to C.038.

Table 20: A compound of formula (Ib) wherein R_1 is cyclohexyl, the bond between carbon atoms 22 and 23 is a single bond, R_2 is $-C(=O)R_4$ and R_3 is hydrogen, and R_4 corresponds to one of the radicals of Table C listed under C.1 to C.038.

Table 21: A compound of formula (Ia) wherein R_1 is 1-methyl-butyl, the bond between carbon atoms 22 and 23 is a double bond, R_2 is $C(=O)R_4$ and R_3 is hydrogen, and R_4 corresponds to one of the radicals of Table C listed under C.1 to C.038.

Table 22: A compound of formula (Ib) wherein R_1 is 1-methyl-butyl, the bond between carbon atoms 22 and 23 is a double bond, R_2 is $-C(=O)R_4$ and R_3 is hydrogen, and R_4 corresponds to one of the radicals of Table C listed under C.1 to C.038.

Table 23: A compound of formula (Ia) wherein R_1 is 1-methyl-butyl, the bond between carbon atoms 22 and 23 is a single bond, R_2 is $C(=O)R_4$ and R_3 is hydrogen, and R_4 corresponds to one of the radicals of Table C listed under C.1 to C.038.

Table 24: A compound of formula (Ib) wherein R_1 is 1-methyl-butyl, the bond between carbon atoms 22 and 23 is a single bond, R_2 is $-C(=O)R_4$ and R_3 is hydrogen, and R_4 corresponds to one of the radicals of Table C listed under C.1 to C.038.

Table D: Compounds of formula (I)

No.	R_2	R_3	retention time (min.)	
			B1a	B1b
D.001	$-CH_2CH_2-$			
D.002	$-CH_2CH_2CH_2-$			
D.003	$-CH_2(CH_2)_3CH_2-$			
D.004	$-CH_2CH_2OCH_2CH_2-$			
D.005	ethyl	ethyl		
D.006	ethyl	methyl		
D.007	allyl	methyl		
D.008	CH_2CH_2OH	methyl		
D.009	$C(O)CH_3$	methyl		
D.010	$C(O)OCH_3$	methyl		
D.011	C(O)Ph	methyl		
D.012	SO_2NH_2	H		
D.013	SO_2NMe_2	H		
D.014	$=N^+=N^-$			
D.015	Benzyl	benzyl		

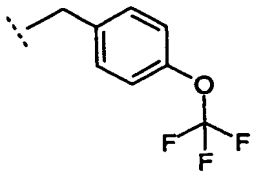
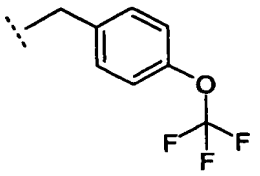
No.	R_2	R_3	retention time (min.)	
			B1a	B1b
D.016				
D.017	(4-methoxyphenyl)methyl	(4-methoxyphenyl)methyl		
D.018	$-CH_2CH_2N(CH_3)CH_2CH_2-$			
D.019	$-CH_2CH_2N(CH_2CH=CH_2)CH_2CH_2-$			
D.020	$-CH_2CH_2N[C(=O)CH_3]CH_2CH_2-$			

Table 25: A compound of formula (Ia) wherein R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between carbon atoms 22 and 23 is a single bond, and the combination of R_2 and R_3 for each compound corresponds to a line D.1 to D.020 of Table D.

Table 26: A compound of formula (Ia) wherein R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between carbon atoms 22 and 23 is a double bond, and the combination of R_2 and R_3 for each compound corresponds to a line D.1 to D.020 of Table D.

Table 27: A compound of formula (Ib) wherein R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between carbon atoms 22 and 23 is a single bond, and the combination of R_2 and R_3 for each compound corresponds to a line D.1 to D.020 of Table D.

Table 28: A compound of formula (Ib) wherein R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between carbon atoms 22 and 23 is a double bond, and the combination of R_2 and R_3 for each compound corresponds to a line D.1 to D.020 of Table D.

Table 29: A compound of formula (Ia) wherein R_1 is cyclohexyl, the bond between carbon atoms 22 and 23 is a single bond, and the combination of R_2 and R_3 for each compound corresponds to a line D.1 to D.020 of Table D.

Table 30: A compound of formula (Ia) wherein R_1 is cyclohexyl, the bond between carbon atoms 22 and 23 is a double bond, and the combination of R_2 and R_3 for each compound corresponds to a line D.1 to D.020 of Table D.

Table 31: A compound of formula (Ib) wherein R_1 is cyclohexyl, the bond between carbon atoms 22 and 23 is a single bond, and the combination of R_2 and R_3 for each compound corresponds to a line D.1 to D.020 of Table D.

Table 32: A compound of formula (Ib) wherein R_1 is cyclohexyl, the bond between carbon

atoms 22 and 23 is a double bond, and the combination of R_2 and R_3 for each compound corresponds to a line D.1 to D.020 of Table D.

Table 33: A compound of formula (Ia) wherein R_1 is 1-methyl-butyl, the bond between carbon atoms 22 and 23 is a single bond, and the combination of R_2 and R_3 for each compound corresponds to a line D.1 to D.020 of Table D.

Table 34: A compound of formula (Ia) wherein R_1 is 1-methyl-butyl, the bond between carbon atoms 22 and 23 is a double bond, and the combination of R_2 and R_3 for each compound corresponds to a line D.1 to D.020 of Table D.

Table 35: A compound of formula (Ib) wherein R_1 is 1-methyl-butyl, the bond between carbon atoms 22 and 23 is a single bond, and the combination of R_2 and R_3 for each compound corresponds to a line D.1 to D.020 of Table D.

Table 36: A compound of formula (Ib) wherein R_1 is 1-methyl-butyl, the bond between carbon atoms 22 and 23 is a double bond, and the combination of R_2 and R_3 for each compound corresponds to a line D.1 to D.020 of Table D.

Formulation Examples for use in crop protection (% = percent by weight)

Example F1: Emulsifiable concentrates	a)	b)	c)
active ingredient	25%	40%	50%
calcium dodecylbenzenesulfonate	5%	8%	6%
castor oil polyethylene glycol ether (36 mol EO)	5%	-	-
tributylphenol polyethylene glycol ether (30 mol EO)	-	12%	4%
cyclohexanone	-	15%	20%
xylene mixture	65%	25%	20%

Mixing finely ground active ingredient and additives gives an emulsifiable concentrate which yields emulsions of the desired concentration on dilution with water.

Example F2: Solutions	a)	b)	c)	d)
active ingredient	80%	10%	5%	95%
ethylene glycol monomethyl ether		20%	-	-
polyethylene glycol (MW 400)		-	70%	-
N-methylpyrrolid-2-one	20%	-	-	-
epoxidised coconut oil	-	-	-	1%
benzine (boiling range: 160-190°)	-	-	94%	-

Mixing finely ground active ingredient and additives gives a solution suitable for use in the form of microdrops.

Example F3: Granules	a)	b)	c)	d)
active ingredient	5%	10%	8%	21%
kaolin	94%	-	79%	54%
highly dispersed silicic acid	1%	-	13%	7%
attapulgite	-	90%	-	18%

The active ingredient is dissolved in dichloromethane, the solution is sprayed onto the carrier mixture and the solvent is evaporated off *in vacuo*.

Example F4: Wettable powders	a)	b)	c)
active ingredient	25%	50%	75%
sodium lignosulfonate	5%	5%	-
sodium lauryl sulfate	3%	-	5%
sodium diisobutylnaphthalenesulfonate	-	6%	10%
octylphenol polyethylene glycol ether (7-8 mol EO)	-	2%	-
highly dispersed silicic acid	5%	10%	10%
kaolin	62%	27%	-

Active ingredient and additives are mixed together and the mixture is ground in a suitable mill, yielding wettable powders that can be diluted with water to form suspensions of the desired concentration.

Example F5: Emulsifiable concentrate

active ingredient	10%
octylphenol polyethylene glycol ether (4-5 mol EO)	3%
calcium dodecylbenzenesulfonate	3%
castor oil polyethylene glycol ether (36 mol EO)	4%
cyclohexanone	30%
xylene mixture	50%

Mixing finely ground active ingredient and additives gives an emulsifiable concentrate which yields emulsions of the desired concentration on dilution with water.

Example F6: Extruder granules

active ingredient	10%
sodium lignosulfonate	2%
carboxymethylcellulose	1%
kaolin	87%

Active ingredient and additives are mixed together, the mixture is ground, moistened with water, extruded and granulated and the granules are dried in a stream of air.

Example F7: Coated granules

active ingredient	3%
polyethylene glycol (MW 200)	3%
kaolin	94%

Uniform application of the finely ground active ingredient to the kaolin moistened with polyethylene glycol in a mixer yields non-dusty coated granules.

Example F8: Suspension concentrate

active ingredient	40%
ethylene glycol	10%
nonylphenol polyethylene glycol ether (15 mol EO)	6%
sodium lignosulfonate	10%
carboxymethylcellulose	1%
aqueous formaldehyde solution (37%)	0.2%
aqueous silicone oil emulsion (75%)	0.8%
water	32%

Mixing finely ground active ingredient and additives gives a suspension concentrate which yields suspensions of the desired concentration on dilution with water.

Biological Examples:

Example B1: Action against Spodoptera littoralis

Young soybean plants are sprayed with an aqueous emulsion spray mixture comprising 12.5 ppm of test compound and, after the spray-coating has dried, the plants are populated with 10 caterpillars of Spodoptera littoralis in the first stage and then placed in a plastics container. 3 days later, the percentage reduction in population and the percentage reduction in feeding damage (% activity) are determined by comparing the number of dead caterpillars and the feeding damage on the treated plants with that on untreated plants.

The compounds of the tables exhibit good activity in this test.

Example B2: Action against Spodoptera littoralis, systemic:

Maize seedlings are placed in the test solution. 6 days later, the leaves are cut off, placed on moist filter paper in a petri dish and infested with 12 to 15 Spodoptera littoralis larvae in the L_1 stage. 4 days later, the percentage reduction in population (% activity) is determined by comparing the number of dead caterpillars on treated plants with that on untreated plants.

The compounds of the tables exhibit good activity in this test.

Example B3: Action against Heliothis virescens

30-35 eggs of Heliothis virescens, from 0 to 24 hours old, are placed on filter paper in a petri dish on a layer of artificial nutrient. 0.8 ml of the test solution is then pipetted onto the filter paper. Evaluation is made 6 days later. The percentage reduction in population (% activity) is determined by comparing the number of dead eggs and larvae on treated plants with that on untreated plants.

The compounds of the tables exhibit good activity in this test.

Example B4: Action against Plutella xylostella caterpillars

Young cabbage plants are sprayed with an aqueous emulsion spray mixture comprising 12.5 ppm of test compound. After the spray-coating has dried, the cabbage plants are populated with 10 caterpillars of Plutella xylostella in the first stage and placed in a plastics container. Evaluation is made 3 days later. The percentage reduction in population and the percentage reduction in feeding damage (% activity) are determined by comparing the number of dead caterpillars and the feeding damage on the treated plants with that on the untreated plants.

The compounds of the tables exhibit good activity in this test. In particular, compounds A.2, A.4, A.12 and A.13 are more than 80 % effective.

Example B5: Activity against Frankliniella occidentalis

In Petri dishes, discs of the leaves of beans are placed onto agar and sprayed with test solution which comprises 12.5 ppm of active compound in a spraying chamber. The leaves are then populated with a mixed population of Frankliniella occidentalis. Evaluation is carried out after 10 days. The reduction in per cent (% activity) is determined by comparing the population on the treated leaves with that of the untreated leaves.

The compounds of the tables exhibit good activity in this test.

Example B6: Action against Diabrotica balteata

Maize seedlings are sprayed with an aqueous emulsion spray mixture comprising 12.5 ppm of the test compound and, after the spray-coating has dried, the maize seedlings are populated with 10 Diabrotica balteata larvae in the second stage and then placed in a plastics container. 6 days later, the percentage reduction in population (% activity) is determined by comparing the number of dead larvae on the treated plants with that on untreated plants.

The compounds of the tables exhibit good activity in this test.

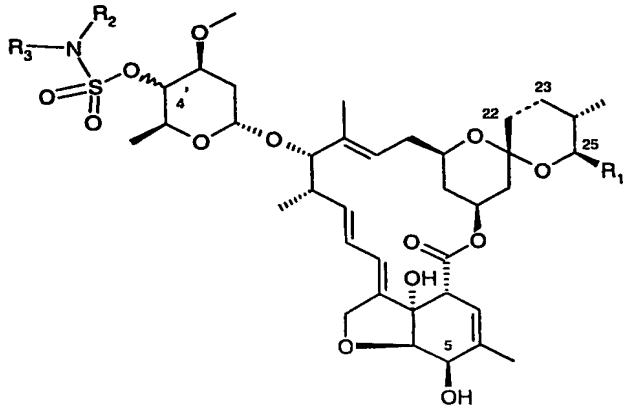
Example B7: Action against Tetranychus urticae

Young bean plants are populated with a mixed population of Tetranychus urticae and sprayed one day later with an aqueous emulsion spray mixture comprising 12.5 ppm of test compound. The plants are incubated for 6 days at 25°C and subsequently evaluated. The percentage reduction in population (% activity) is determined by comparing the number of dead eggs, larvae and adults on the treated plants with that on untreated plants.

The compounds of the tables exhibit good activity in this test. In particular, compounds A.2 to A.4, A.12 and A.13 are more than 80 % effective.

What is claimed is:

1. A compound of formula



(I)

wherein the bond marked by ~~ indicates the S- as well as the R-isomer at the 4'-position; and wherein the bond between carbon atoms 22 and 23 may be a single or a double bond;

R_1 is C_1-C_{12}alkyl, C_3-C_8cycloalkyl; or C_2-C_{12}alkenyl;

R_2 and R_3 are independently of each other hydrogen, C_1-C_{12}alkyl, C_3-C_{12}cycloalkyl, C_2-C_{12}alkenyl, C_2-C_{12}alkynyl, aryl or heteroaryl; wherein the C_1-C_{12}alkyl, C_3-C_{12}cycloalkyl, C_2-C_{12}alkenyl, C_2-C_{12}alkynyl, aryl and heteroaryl radicals may be unsubstituted or mono- to penta-substituted; -C(=O)R_4 or SO_2R_4; or

R_2 and R_3 together are a three- to seven-membered alkylene bridge or a four- to seven-membered alkenylene bridge wherein one or two CH_2 groups in the alkylene or alkenylene may have been replaced by O, S or NR_5; or are a group $=N^+=N^-$,

and wherein the substituents of the alkyl, alkenyl, alkynyl, alkylene, alkenylene, cycloalkyl, aryl and heteroaryl radicals defined under R_2 and R_3 are selected from the group consisting of OH, =O, SH, =S, -NH_2, CN, NO_2, halogen, C_1-C_{12}alkyl, halo-C_1-C_2alkyl, C_1-C_{12}alkenyl, C_2-C_6alkynyl; C_3-C_8cycloalkyl which is unsubstituted or substituted by from one to three methyl groups; norbornenyl; C_3-C_8cycloalkenyl that is unsubstituted or substituted by from one to three methyl groups; C_3-C_8halocycloalkyl, C_1-C_{12}alkoxy, C_1-C_6-alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_{12}alkenyloxy, C_2-C_{12}alkenyloxy-C_1-C_6alkoxy, C_3-C_8cycloalkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_3-C_8cycloalkylthio, C_1-C_{12}haloalkylthio, C_1-C_{12}alkylsulfinyl, C_3-C_8cycloalkyl-

sulfinyl, C_1-C_{12}haloalkylsulfinyl, C_3-C_8halocycloalkylsulfinyl, C_1-C_{12}alkylsulfonyl, C_3-C_8cycloalkylsulfonyl, C_1-C_{12}haloalkylsulfonyl, C_3-C_8halocycloalkylsulfonyl, C_2-C_8alkenyl, C_2-C_8alkynyl, -NH(C_1-C_6alkyl), -N(C_1-C_6alkyl)$_2$, -C(=O)R_6, -NHC(=O)R_7, -P(=O)(OC_1-C_6alkyl)$_2$, aryl, heterocyclyl, aryloxy and heterocyclyloxy; wherein the aryl, heterocyclyl, aryloxy and heterocyclyloxy radicals are unsubstituted or, depending upon the possibilities of substitution at the ring, mono- to penta-substituted by substituents selected from the group consisting of OH, halogen, CN, NO_2, C_1-C_{12}alkyl, C_3-C_8cycloalkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_{12}alkylsulfinyl, C_1-C_{12}alkylsulfonyl, C_1-C_6alkoxy-C_1-C_6alkyl, dimethylamino-C_1-C_6alkoxy, C_2-C_8alkenyl, C_2-C_8alkynyl, phenoxy, phenyl-C_1-C_6alkyl; phenoxy that is unsubstituted or substituted by from one to three substituents selected independently of one another from halogen, methoxy, trifluoromethyl and trifluoromethoxy; phenyl-C_1-C_6alkoxy that is unsubstituted or substituted in the aromatic ring by from one to three substituents selected independently of one another from halogen, methoxy, trifluoromethyl and trifluoromethoxy; phenyl-C_2-C_6alkenyl, phenyl-C_2-C_6alkynyl, methylenedioxy, -C(=O)R_6, -O-C(=O)R_7, -NH-C(=O)R_7, -NH_2, -NH(C_1-C_{12}alkyl), -N(C_1-C_{12}alkyl)$_2$, C_1-C_6alkylthio, C_1-C_6alkylsulfinyl, C_3-C_8cycloalkylsulfinyl, C_1-C_6haloalkylsulfinyl, C_3-C_8halocycloalkylsulfinyl, C_1-C_6alkylsulfonyl, C_3-C_8cycloalkylsulfonyl, C_1-C_6haloalkylsulfonyl and C_3-C_8halocycloalkylsulfonyl;

R_4 is H, C_1-C_8alkyl, C_1-C_8alkyl that is mono- to hepta-substituted by halogen, nitro, C_1-C_8alkoxy, aryloxy, OH, SH, -NH_2, -NH(C_1-C_{12}alkyl) or -N(C_1-C_{12}alkyl)$_2$; C_1-C_8alkoxy, halo-C_1-C_8alkoxy, C_3-C_8cycloalkyl, C_3-C_8cycloalkoxy, C_2-C_8alkenyl, halo-C_2-C_8alkenyl, C_2-C_8alkenyloxy, halo-C_2-C_8alkenyloxy, C_2-C_8alkynyl, C_2-C_8alkynyloxy, -NH_2, -NH(C_1-C_{12}alkyl), -N(C_1-C_{12}alkyl)$_2$, aryl, aryloxy, benzyl, benzyloxy, heterocyclyl, heterocyclyloxy, heterocyclylmethyl, heterocyclylmethoxy, -NH-aryl, -NH-heterocyclyl, -N(C_1-C_6alkyl)-aryl or -N(C_1-C_6alkyl)-heterocyclyl; wherein the radicals aryl, aryloxy, benzyl, benzyloxy, heterocyclyl, heterocyclyloxy, heterocyclylmethyl, heterocyclylmethoxy, -NH-aryl, -NH-heterocyclyl, -N(C_1-C_6alkyl)-aryl and -N(C_1-C_6alkyl)-heterocyclyl are unsubstituted or, depending upon the possibilities of substitution at the ring, are in the ring substituted by from one to three substituents selected independently of one another from halogen, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_{12}alkylsulfinyl, C_1-C_{12}alkylsulfonyl, C_2-C_8alkenyloxy, C_2-C_8alkynyloxy, nitro, -N_3, and cyano;

R_5 is C_1-C_8alkyl, C_3-C_8cycloalkyl, C_2-C_8alkenyl, C_2-C_8alkynyl, benzyl, -C(=O)-R_8 or -C(=S)-R_8;

R_6 is H, OH, SH, C_1-C_8alkyl, C_1-C_8alkyl which is mono- to hepta-substituted by halogen, nitro, C_1-C_8alkoxy, aryloxy, OH, SH, $-NH_2$, $-NH(C_1$-C_{12}alkyl) or $-N(C_1$-C_{12}alkyl)$_2$; C_1-C_8alkoxy, halo-C_1-C_8alkoxy, C_3-C_8cycloalkyl, C_3-C_8cycloalkoxy, C_2-C_8alkenyl, C_2-C_8alkenyloxy, C_2-C_8alkynyl, C_2-C_8alkynyloxy, $-NH_2$, $-NH(C_1$-C_{12}alkyl), $-N(C_1$-C_{12}alkyl)$_2$, aryl, aryloxy, benzyl, benzyloxy, heterocyclyl, heterocyclyloxy, heterocyclylmethyl or heterocyclylmethoxy; wherein the radicals aryl, aryloxy, benzyl, benzyloxy, heterocyclyl, heterocyclyloxy, heterocyclylmethyl and heterocyclylmethoxy are unsubstituted or, depending upon the possibilities of substitution at the ring, are substituted by from one to three substituents selected independently of one another from halogen, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_{12}alkylsulfinyl, C_1-C_{12}alkylsulfonyl, C_2-C_8alkenyloxy, C_2-C_8alkynyloxy, nitro, $-N_3$, and cyano;

R_7 is H, C_1-C_{12}alkyl, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_{12}haloalkyl, C_2-C_8alkenyl, C_2-C_8alkynyl, aryl, heterocyclyl, benzyl, $-NH_2$, $-NH(C_1$-C_{12}alkyl), $-N(C_1$-C_{12}alkyl)$_2$, -NH-phenyl or $-N(C_1$-C_{12}alkyl)-phenyl; and

R_8 is H, OH, SH, $-NH_2$, $-NH(C_1$-C_{12}alkyl), $-N(C_1$-C_{12}alkyl)$_2$, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_{12}alkylthio, C_1-C_{12}alkylsulfinyl, C_1-C_{12}alkylsulfonyl, C_2-C_8alkenyloxy, C_2-C_8alkynyloxy; phenyl, phenoxy, benzyloxy, -NH-phenyl, $-N(C_1$-C_6alkyl)-phenyl, $-NH$-C_1-C_6alkyl-C(=O)-R_9, $-N(C_1$-C_6alkyl)-C_1-C_6alkyl-C(=O)-R_9; or phenyl, phenoxy, benzyloxy, -NH-phenyl or $-N(C_1$-C_6alkyl)—phenyl each of which is substituted in the aromatic ring by from one to three substituents selected independently of one another from halogen, C_1-C_6alkoxy, C_1-C_6haloalkyl and C_1-C_6haloalkoxy;

R_9 is H, OH, C_1-C_{12}alkyl, C_1-C_{12}alkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy, C_2-C_8alkenyloxy, phenyl, phenoxy, benzyloxy, $-NH_2$, $-NH(C_1$-C_{12}alkyl), $-N(C_1$-C_{12}alkyl)$_2$, -NH-phenyl or $-N(C_1$-C_{12}alkyl)-phenyl;

and, where applicable, to E/Z isomers, mixtures of E/Z isomers, diastereomers and/or tautomers, in each case in free form or in salt formand, where applicable, to E/Z isomers, mixtures of E/Z isomers and/or tautomers, in each case in free form or in salt form.

2. A pesticidal composition comprising as active ingredient at least one compound of formula (I) as described in claim 1, and at least one adjuvant.

3. A method of controlling pests, which comprises applying a composition as described in claim 2 to the pests or to the locus thereof.

4. A process for the preparation of a composition comprising at least one adjuvant, as described in claim 2, which comprises intimately mixing and/or grinding the active ingredient with the adjuvant(s).

5. Use of a compound of formula (I) as described in claim 1 in the preparation of a composition as described in claim 2.

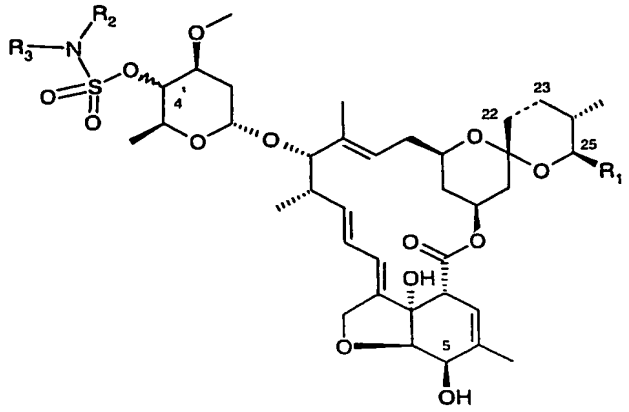
6. Use of a composition as described in claim 2 in controlling pests.

7. A method according to claim 3 for the protection of plant propagation material, which comprises treating the propagation material or the planting site of the propagation material.

8. Plant propagation material treated in accordance with the method described in claim 7.

Abstract of the Disclosure

A compound of formula



(I)

wherein the bond marked by ~~ indicates either the S or the R isomer at the 4'-position; and wherein the bond between carbon atoms 22 and 23 may be a single or a double bond;

R_1 is C_1-C_{12}alkyl, C_3-C_8cycloalkyl; or C_2-C_{12}alkenyl;

R_2 is, for example, hydrogen, unsubstituted or mono- to penta-substituted C_1-C_{12}alkyl or unsubstituted or mono- to penta-substituted C_2-C_{12}alkenyl;

R_3 is, for example, hydrogen, C_1-C_{12}alkyl, mono- to penta-substituted C_1-C_{12}alkyl, unsubstituted or mono- to penta-substituted C_3-C_{12}cycloalkyl or unsubstituted or mono- to penta-substituted C_2-C_{12}alkenyl;

and wherein the substituents of the alkyl, alkenyl, alkynyl, alkylene, alkenylene and cycloalkyl radicals defined under R_2 and R_3 are selected, for example, from the group consisting of OH, halogen, halo-C_1-C_2alkyl, CN, NO_2 and C_2-C_6alkynyl;

and, where applicable, E/Z isomers, mixtures of E/Z isomers and/or tautomers, in each case in free form or in salt form; a process for the preparation of and the use of those compounds, their isomers and tautomers; starting materials for the preparation of the compounds of formula (I); pesticidal compositions in which the active ingredient has been selected from those compounds and their tautomers; and a method of controlling pests using those compositions are described.